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**A RESEARCH STUDY ON INTERNAL  
CORROSION OF HIGH PRESSURE BOILERS**

**FINAL PROGRESS REPORT**

by

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*This is the third and final report from an investigation being performed under the sponsorship of the American Society of Mechanical Engineers with joint financial support by the Edison Electric Institute, Industry, and others concerned with the operation of high pressure boilers.*

**Presented at**

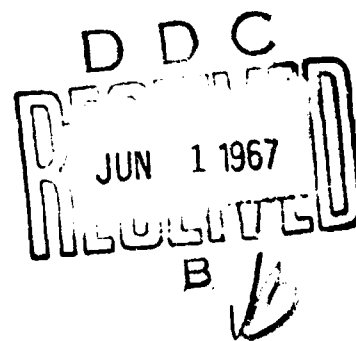
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#### ABSTRACT

The following report is the third and final in a series describing the progress of "A RESEARCH STUDY ON INTERNAL CORROSION OF HIGH PRESSURE BOILERS". The first report described the background, scope, and organization of the program as well as the test facility. The second report discussed the methods of testing and the results of the first six runs. This final report describes the results of the last six tests and discusses the conclusions drawn from all of Phases II and III. The scope and an outline of seven tests composing the newly scheduled Phase IV program are also included.

The results of runs with three types of boiler water treatment, fouled heat transfer surfaces, and conditions simulating fresh water and seawater condenser leakage are included. Data relating to deposition and corrosion in these environments are presented with particular emphasis on the severe corrosion experienced with simulated seawater condenser leakage.

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## INTRODUCTION

The first and second progress reports considered the general background of the investigation, defined the scope of the program and the philosophy of testing, and described the test apparatus and experimental procedures. Table I summarizes the program's experimental conditions in terms of boiler water treatment and types of contaminants for both the Phase II and III tests already completed, and the new Phase IV tests to be run during 1967. The results of Phase II and III-A were discussed in the second progress report. This final report describes the results of the Phase III, Group B and C tests, and includes the conclusions drawn from the entire program.

The tests discussed by this report were designed to study the effects of both fresh water and seawater condenser leakage upon the corrosion of boiler tubing fouled with preboiler corrosion products. These runs were made with three types of boiler water treatment and the same severe heat transfer conditions previously employed.

The goals of Phase IV are: (1) to obtain additional information on corrosion resulting from boiler water contaminated by fresh water condenser leakage, (2) to determine the causes of hydrogen damage and (3) to study whether heat transfer conditions beyond the threshold of departure from nucleate boiling can contribute to corrosion. Phase IV is sponsored and contracted separately from Phases II and III.

## APPARATUS AND TEST PROCEDURES

The apparatus and operating parameters for these tests were the same as those employed during Phases II and III-A. Figure 1 is a schematic diagram of the corrosion test loop and Tables II and III summarize the chemical and mechanical operating parameters employed throughout the program.

The terms "fresh water condenser leakage" and "seawater condenser leakage" used throughout this report, refer to the contaminant solutions employed to simulate condenser leakage as described in the following procedures. The reference to "dirty boiler conditions" or "corrosion product contaminants", describes the 1:1 mixture of magnetite and copper powder used to simulate the condition of a boiler with heat transfer surfaces fouled by an accumulation of preboiler and boiler corrosion products. Details relating to these materials were included in the second progress report.

### *Operating Procedure for Tests with Fresh Water Condenser Leakage (Tests 1, 2, 3 — Phase III — Group B)*

Both preboiler corrosion products and fresh water condenser leakage were employed during this group of tests. Injection of corrosion products was made on a 2-hour cycle during the first several days of operation, and at various intervals thereafter until 2,800 to 3,400 grams of contaminant had been added. Daily additions of fresh water condenser leakage were made throughout each 14-day run. Contaminant salt solutions were

TABLE I  
PROGRAM ORGANIZATION

Phase No.	Group	Test No.	Treatment	Boiler Condition	Boiler Water Contamination
II	—	1	Volatile	Clean	None
		2	Phosphate	Clean	None
		3	Caustic	Clean	None
III	A	1	Volatile	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	None
		2	Phosphate	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	None
		3	Caustic	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	None
	B	1	Volatile	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	Fresh water salts
		2	Phosphate	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	Fresh water salts
		3	Caustic	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	Fresh water salts
	C	1	Volatile	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	Seawater salts
		2	Phosphate	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	Seawater salts
		3	Caustic	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	Seawater salts
IV	A	1	Volatile	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	Fresh water salts
		2	Phosphate	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	Fresh water salts
		3	Caustic	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	Fresh water salts
	B	1	Volatile	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	Other salts
		2	Phosphate	Dirty—Fe <sub>3</sub> O <sub>4</sub> + Cu	Other salts
	C	1	Volatile	Clean	Tests in DNB
		2	Phosphate	Clean	Tests in DNB

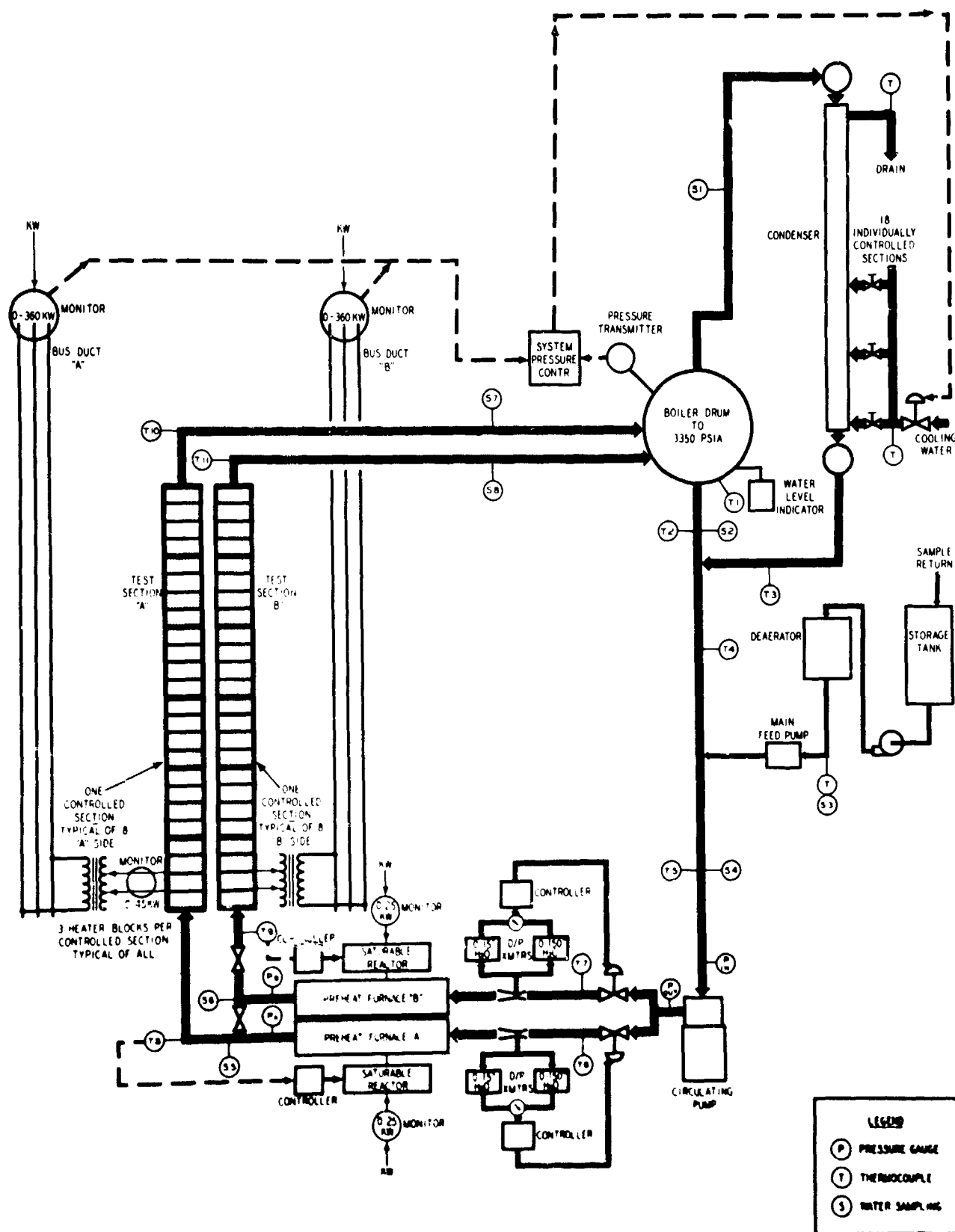


Fig. 1: Schematic arrangement of the heat transfer and corrosion test loop

TABLE II  
WATER SPECIFICATIONS FOR 2600 PSIG

Name Treating Chemical	pH Value at 25 C	Hydroxide ppm OH	Phosphate ppm PO <sub>4</sub>
VOLATILE (NH <sub>3</sub> )	8.6-9.0	0	0
PHOSPHATE (Na <sub>3</sub> PO <sub>4</sub> )	9.8-10.0	0	9-11
CAUSTIC (NaOH)	10.5-10.7	AS REQUIRED TO MAINTAIN pH	2-4

injected at the bottom of the vertical preheat sections to minimize deposition on the surfaces of the horizontal preheater (not instrumented for temperature measurements). The amount and composition of the contaminants, added during each 8-hour period of simulated condenser leakage, are as follows:

Quantity — 40 liters

Concentration — 200 ppm

Composition: — Calcium sulfate — 30 ppm  
Magnesium sulfate — 20 ppm  
Calcium bicarbonate — 70 ppm  
Sodium sulfate — 40 ppm  
Sodium chloride — 35 ppm  
Sodium silicate — 5 ppm

No attempt was made to maintain nominal boiler water control conditions during these periods, although treatment chemicals were added to the loop at the rate normally used to compensate for depletion of concentration due to sampling losses. Control conditions were re-established after each period of simulated leakage by injecting treatment chemicals and by blowdown.

#### Operating Procedure for Tests with Seawater Condenser Leakage (Tests 1, 2, 3 — Phase III — Group C)

The amount of contaminant salts and the procedure for chemical control was modified for the tests with

seawater condenser leakage. These changes in procedure were made to obtain greater deposition and a more aggressive environment than were experienced during the fresh water runs. The increase in concentration of the contaminant solution provided a three-fold increase in total calcium and magnesium content. Seawater condenser leakage of the following composition and quantity was added each day:

Quantity — 40 liters

Concentration — 1,578 ppm

Composition: — Sodium chloride — 1074 ppm  
Magnesium chloride — 228 ppm  
Sodium sulfate — 179 ppm  
Calcium chloride — 51 ppm  
Potassium chloride — 30 ppm  
Sodium bicarbonate — 9 ppm  
Potassium bromide — 4 ppm  
Boric acid — 1 ppm  
Strontium chloride — 1 ppm  
Others — 1 ppm

Stock solutions for the above were made in accordance with the ASTM Standard Specifications for Substitute Ocean Water (D1141-52) including heavy metal constituents.

The modified chemical control procedure for the seawater tests specified that no treatment chemicals were to be added to the boiler water during periods of contaminant injection, thereby simulating an undetected condenser leak. This permitted pH, conductivity, and treatment chemical residuals to vary. Control conditions were re-established after each daily eight hour period of simulated leakage.

## RESULTS

In evaluating the results of this research program, it must be kept in mind that the test conditions employed were intended to accelerate corrosion rather than

TABLE III  
NOMINAL TEST CONDITIONS

NOMINAL TEST CONDITION	A	B
Mass Velocity (G) = lbs/hr-ft <sup>2</sup>	0.55 × 10 <sup>4</sup>	0.55 × 10 <sup>4</sup>
Flow Rate (W) = lbs/hr	3,630	3,630
*Heat Flux (Q/A) <sub>1</sub> = BTU/hr-ft <sup>2</sup> (based on ID of tube)	150,000	150,000
Heat Flux (Q/A) <sub>1</sub> = BTU/hr-ft <sup>2</sup> (based on projected area)	173,000	173,000
**Approx. Heat Flux (Q/A) <sub>2</sub> = BTU/hr-ft <sup>2</sup> (based on ID of tube)	110,000	110,000
Approx. Heat Flux (Q/A) <sub>2</sub> = BTU/hr-ft <sup>2</sup> (based on projected area)	127,000	127,000
Approx. Total Preheat (Q) = BTU/hr	280,000	97,000
***Approx. Preheat Flux (Q/A) = BTU/hr-ft <sup>2</sup>	121,500	42,000
Approx. Quality (X <sub>e</sub> ) Entering Test Section	23%	8%
Approx. Quality X <sub>1</sub> Leaving (Q/A) <sub>1</sub>	30%	15%
Approx. Quality X <sub>2</sub> Leaving (Q/A) <sub>2</sub>	35%	20%

\* (Q/A)<sub>1</sub> Heat flux in lower test section

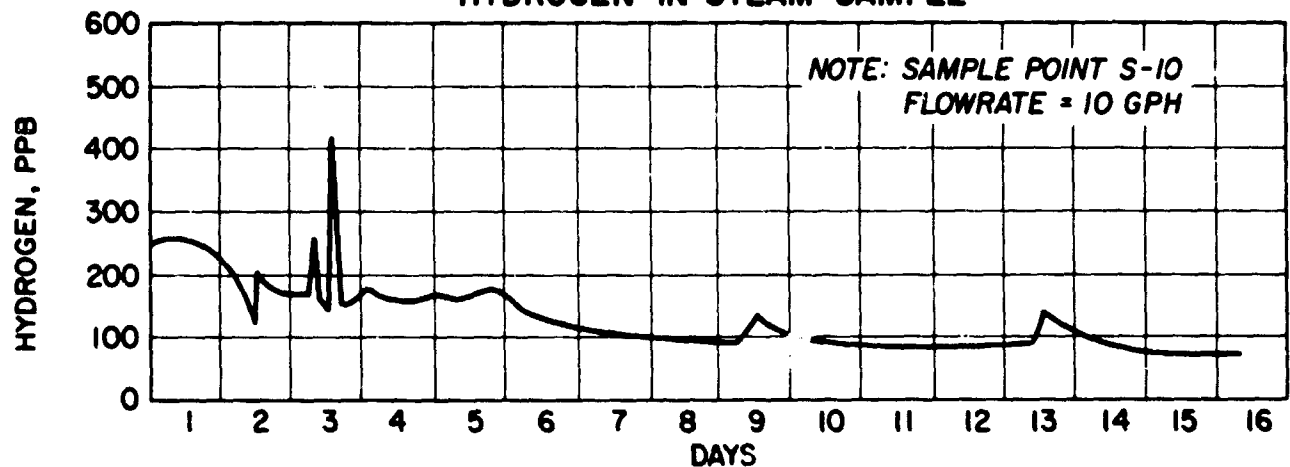
\*\* (Q/A)<sub>2</sub> Heat flux in upper test section

\*\*\*These fluxes are based on the entire 16 feet of vertical preheat

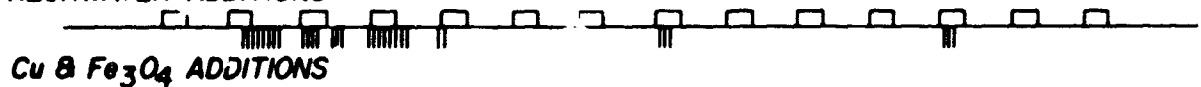
TABLE IV  
SUMMARY OF RESULTS

	Test 1	Group B Test 2	Test 3	Test 1	Group C Test 2	Test 3
General						
BW Treatment	NH <sub>3</sub>	FO <sub>4</sub>	OH	NH <sub>3</sub>	PO <sub>4</sub>	OH
Fe <sub>3</sub> O <sub>4</sub> + Cu, Gm	3000	2800	3400	500	2800	3000
FW salts, Gm	112	112	112	—	—	—
SW salts, Gm	—	—	—	126	693	882
Corrosion						
Penetration, mils	Trace	Trace	Trace	6(2 days)	3	10
Metallurgical	No change	No change	No change	No change	No change	No change
Deposits						
Thickness, mils	8	5	5	25	40	45
Weight A loop/B loop						
Gm/linear ft	0.9/1.2	1.0/0.7	0.9/1.1	0.7/2.4	7.4/1.4	4.6/2.7
Temp rise max, F	27	20	33	14	96	30
Chemical Composition	CaSO <sub>4</sub> Fe <sub>2</sub> O <sub>3</sub> Fe <sub>3</sub> O <sub>4</sub> Al <sub>2</sub> O <sub>3</sub> ·Na <sub>2</sub> O·6SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub> Fe <sub>3</sub> O <sub>4</sub> Cu Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub> Fe <sub>2</sub> O <sub>3</sub> Cu	Mg(OH) <sub>2</sub> Fe <sub>3</sub> O <sub>4</sub> CaSO <sub>4</sub> 3MgO·2SiO <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub> Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub> Cu Fe <sub>2</sub> O <sub>3</sub>

TEST 1B PHASE III 3/21/66 - 4/5/66  
HYDROGEN IN STEAM SAMPLE



FRESHWATER ADDITIONS



TEST 1B PHASE III 3/21/66 - 4/5/66  
TUBE CROWN TEMPERATURE INCREASE

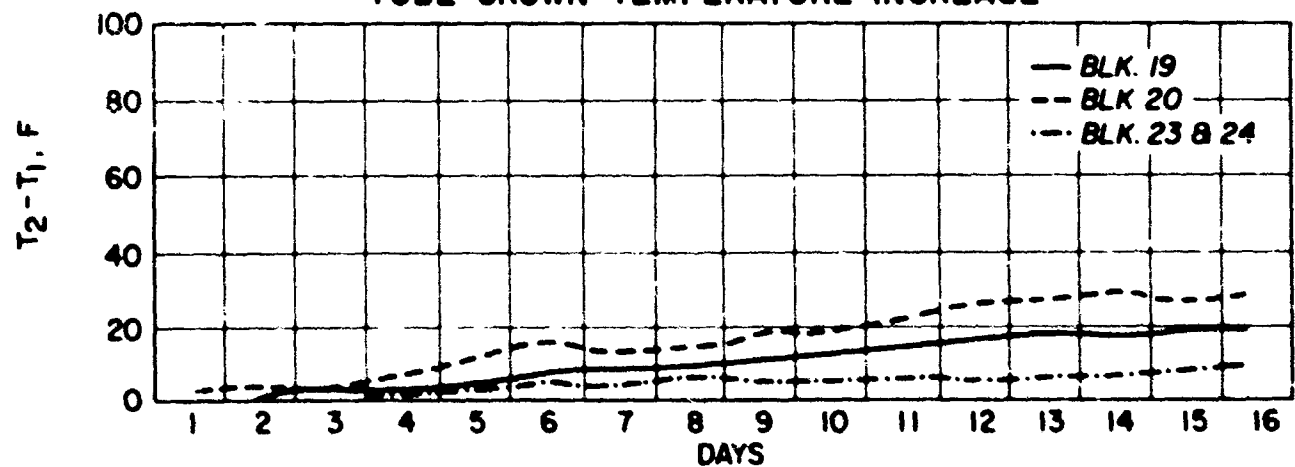


Fig. 2

to duplicate typical boiler operation. Detailed results including a chronological log of the events and data from each test are included in the following subsections. Some of these data are summarized in Table IV.

#### Log — Test 1B, Phase III

Volatile ( $\text{NH}_3$ ) Boiler Water Treatment — pH = 8.6 to 9.0

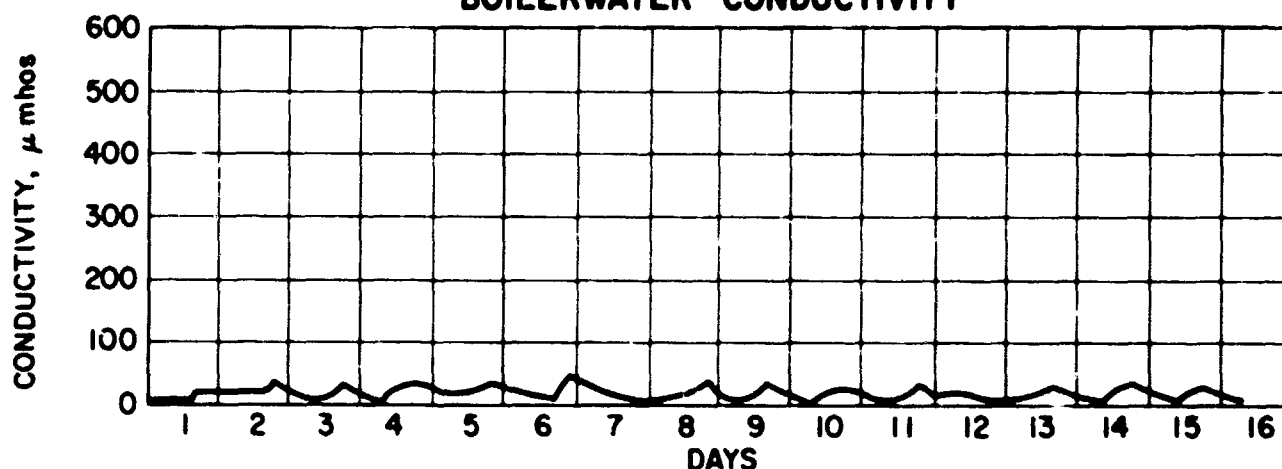
Dirty Boiler Conditions — Fresh Water Condenser Leakage

The test loop had been chemically cleaned immediately preceding this test, hence the need for a period of "seasoning" operation was anticipated. However, hydrogen concentrations failed to reach equilibrium after operating for three days with ammonia with pH

values as high as 10.0, thereby indicating a very slow rate of surface passivation. Contaminant salt injection was begun at this time. This initial contaminant injection maintained boiler water pH at 10.0 without ammonia addition, and resulted in a reduction in hydrogen evolution. On the following day, (Figs. 2 and 3) additional fresh water salts were added and iron oxide and copper additions were begun.

Once the series of iron oxide and copper contaminant additions had been completed, the hydrogen concentration stabilized at approximately 100 ppb. (Fig. 2). Subsequent injections of iron oxide and copper produced short duration increases in hydrogen concentration, however, values remained close to 100 ppb throughout most of the test. Figure 3 shows that each daily intro-

### TEST 1B PHASE III 3/21/66 - 4/5/66 BOILERWATER CONDUCTIVITY



#### FRESHWATER ADDITIONS



### TEST 1B PHASE III 3/21/66 - 4/5/66 BOILERWATER pH

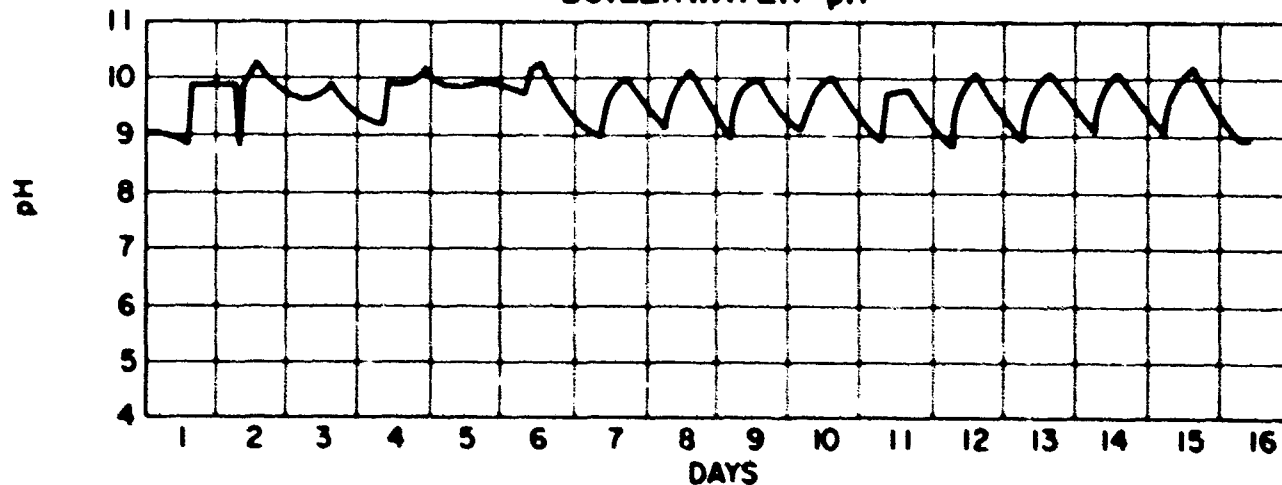


Fig. 3

TABLE V  
TEST 1B—PHASE III

DEPOSIT DISTRIBUTION				
Loop	Q/A-Btu/hr-ft <sup>2</sup>	Heated/Unheated Side	Block Location	Gm/Linear Ft
A	150,000	Heated	20	0.831
A	150,000	Heated	19	0.893
A	150,000	Heated	18	0.770
A	150,000	Heated	17	0.731
B	150,000	Heated	20	1.169
B	150,000	Heated	19	1.166
B	150,000	Heated	17	0.781
B	—	Unheated	20	0.560
B	—	Unheated	19	0.503
B	—	Unheated	17	0.289

Note: No appreciable amount of deposit could be removed from the unheated portion of tubing at Blocks 17A to 20A.

#### DEPOSIT ANALYSIS

		A Loop	B Loop
X-ray Diffraction	Major, > 30%	CaSO <sub>4</sub>	CaSO <sub>4</sub>
	Lo Major, 20 to 30%	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
	Minor, 8 to 15%	Al <sub>2</sub> O <sub>3</sub> ·Na <sub>2</sub> O·6SiO <sub>2</sub> , Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>
Spectrography	Major, > 15%	Fe, Ca	Fe, Ca
	Lo Major, 8 to 15%	Si	
	Minor, 3 to 8%		Si
	Lo Minor, 1 to 3%	Al, Mg, Na, Cu	Mg, Cu
Chemical Analysis, %	SO <sub>3</sub>	22	26
	CO <sub>2</sub>	est. < 1	Neg.
	P <sub>2</sub> O <sub>5</sub>	< 1	1
	SiO <sub>2</sub>	13	6
	Fe <sub>2</sub> O <sub>3</sub>	32	40
	CaO	25	22
	MgO	2	2
	Na <sub>2</sub> O	2	
	Cu	1	3
	Al <sub>2</sub> O <sub>3</sub>	3	

Unheated side deposits were Fe<sub>3</sub>O<sub>4</sub> and Cu + trace elements

Drum deposits were Fe<sub>3</sub>O<sub>4</sub> and Cu + trace elements

duction of fresh-water-contaminant salts resulted in a pH elevation from 9.0 to levels slightly in excess of 10.0, and a conductivity increase from approximately 2.0 to 35.0. Boiler water analyses during periods of simulated condenser leakage revealed water chemistry variations from essentially zero solids to the following typical peak solids concentrations:

Sodium	6.0 ppm
Calcium	Trace
Magnesium	Trace
Chloride	1.6 ppm
Silica	0.2 ppm
Sulfate	2.7 ppm
Carbon dioxide	5.1 ppm
Ammonia	0.01 ppm

Boiler water blowdown was used to re-establish normal control conditions after each period of addition.

Increases in tube crown temperature due to deposit formation were experienced during this test. A maximum temperature elevation of approximately 30 F was experienced at Block 20 A.

Inspection of the test sections revealed that the internal surfaces were covered with 7.5 mils (maximum) of very dense tenacious deposit. (Figs. 4 and 5). The deposit distribution and composition are shown in Table V.

Chemical cleaning of specimens for removal of this deposit was difficult; however, several hours soaking in



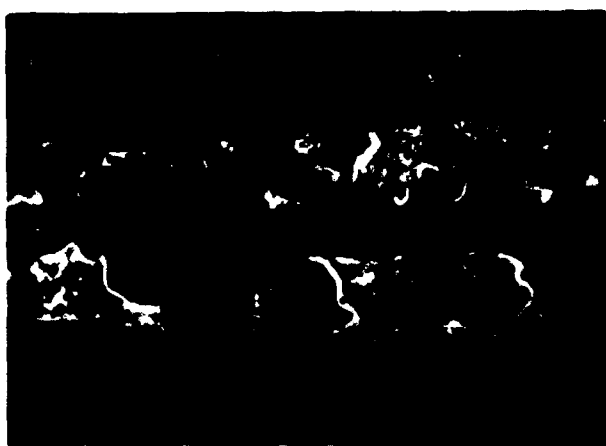


Fig. 4: Upper—Appearance of deposits formed on tube surfaces during Test 18

Lower—Tube surface after removal of deposits by chemical cleaning



Fig. 5: 100X photomicrograph of the deposit cross section from Test 18

hot (160 F) inhibited 5 percent hydrochloric acid, 0.5 percent ammonium bifluoride, and 1 percent thiourea solution eventually loosened deposits sufficiently for removal. Inspection of the underlying metal revealed no measurable corrosion. Metallurgical examination revealed no changes in structure.

### Log-Test 2B, Phase III

Coordinated Phosphate Boiler Water Treatment —  
pH = 9.8 to 10.0

Dirty Boiler Conditions — Fresh Water Condenser  
Leakage

An equilibrium hydrogen concentration of approximately 65 ppb was reached shortly after start-up (Fig. 6). Subsequently, fresh-water-contaminant-salt injection was started and the addition of iron oxide and copper was begun several hours later. Fresh-water-condenser leakage resulted in small increases in boiler water conductivity; however, no change in pH was experienced (Fig. 7). Boiler water analyses during periods of simulated condenser leakage revealed water chemistry variations to peak levels as shown in the following:

pH	10.0
Sodium	7.0 ppm
Calcium	negative
Magnesium	negative
Chloride	1.5 ppm
Silica	0.5 ppm
Sulfate	6.0 ppm
Phosphate	4.0 ppm
Carbon dioxide	2.5 ppm

No increases in hydrogen evolution resulted from the injection of fresh water salts. The maximum tube metal temperature increase of 20 F occurred at Block 20 A. During shutdown of the loop, phosphate concentrations increased as shown by Fig. 8.

Examination of the test sections revealed that the internal surfaces were covered with up to 5 mils of relatively loose, porous deposits (Figs. 9 and 10). Table VI shows the distribution and analysis of this material. The deposit was readily removed by soaking in the standard hydrochloric acid and thiourea solution, and the underlying metal was found to have experienced no measurable corrosion. Metallurgical examination revealed no changes in the metal structure.

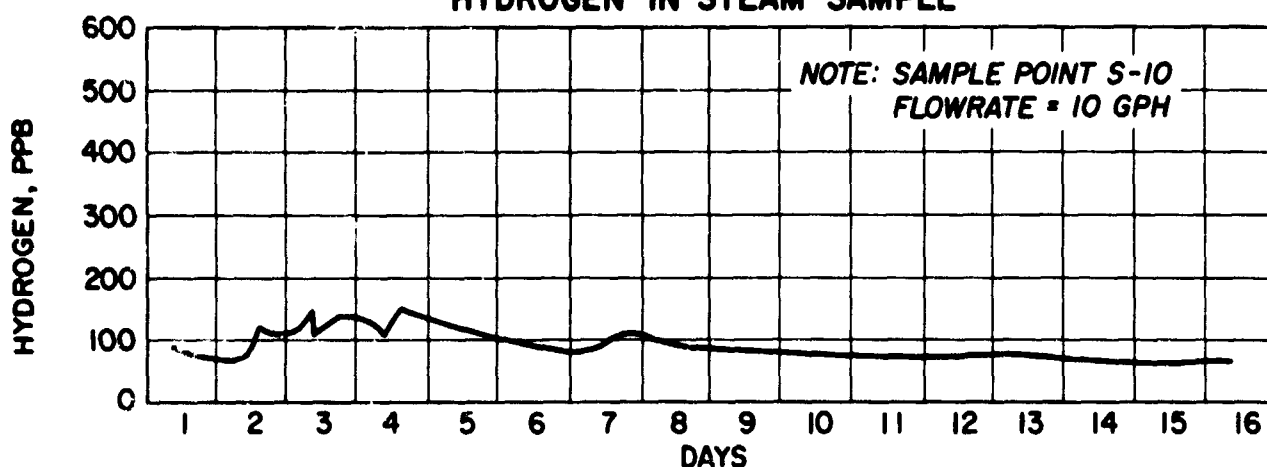
### Log Test 3B Phase III

Free Caustic Boiler Water Treatment pH = 10.5  
to 10.7

Dirty Boiler Conditions — Fresh Water Condenser  
Leakage

A base hydrogen concentration of approximately 75 ppb was reached shortly after start-up (Fig. 11). Subsequently, fresh-water-contaminant injection was started and shortly thereafter additions of iron oxide and copper were begun. Fresh-water-contaminant injection resulted in small increases in boiler water conductivity with no

### TEST 2B PHASE III 5/24/66 - 6/9/66 HYDROGEN IN STEAM SAMPLE



#### FRESHWATER ADDITIONS

#### Cu & Fe<sub>2</sub>O<sub>4</sub> ADDITIONS

### TEST 2B PHASE III 5/24/66 - 6/9/66 TUBE CROWN TEMPERATURE RISE

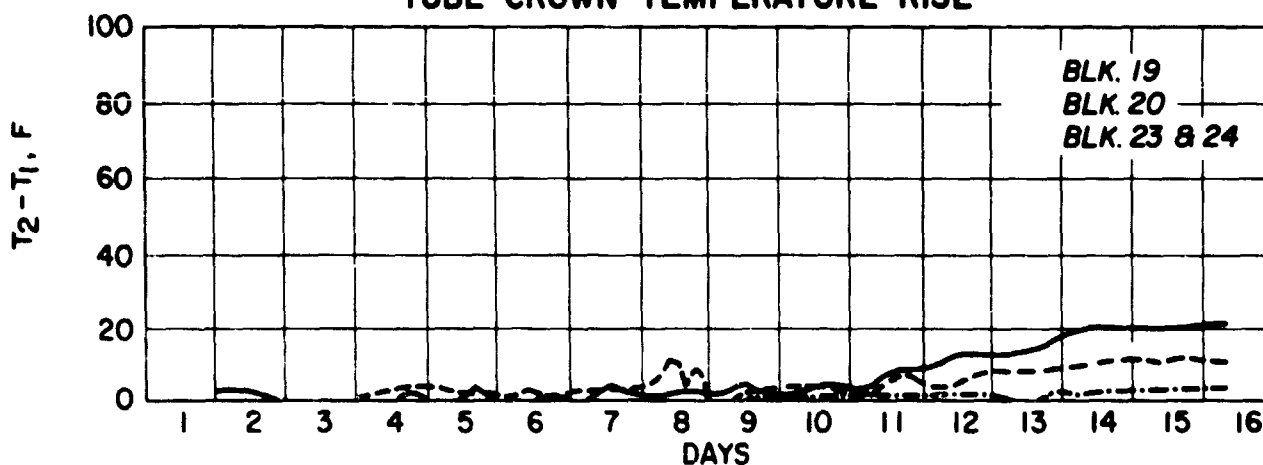


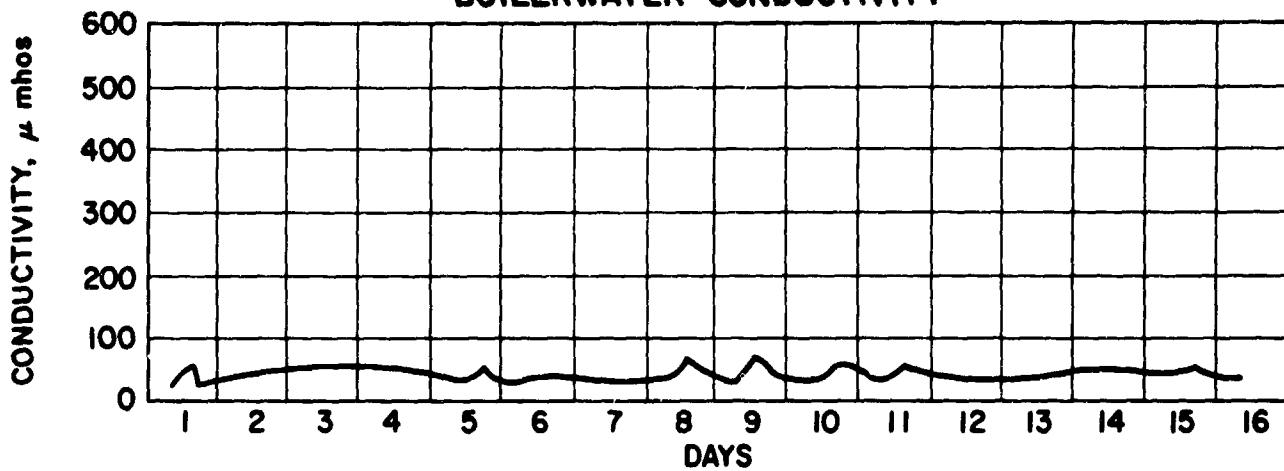
Fig. 6

significant variation in pH (Fig. 12). Boiler water analyses during periods of condenser leakage revealed water chemistry variations with typical peak solids concentrations as shown by the following:

pH	10.6
Sodium	13.9 ppm
Calcium	Trace
Magnesium	Negative
Chloride	2.8 ppm
Sulfate	2.0 ppm
Silica	0.3 ppm
Phosphate	Trace
Carbon dioxide	5 ppm

Injectons of iron oxide and copper elevated hydrogen concentrations to approximately 250 ppb for short periods; however, fresh water condenser leakage produced no increases in hydrogen concentration. Reflux condenser hydrogen values were 100 ppb or less throughout most of the run. A maximum tube metal temperature increase of 30 F occurred at Block 20 A. During shutdown of the loop, phosphate concentrations increased (Fig. 13). Examination of the test sections revealed that the internal surfaces were covered with up to 5 mils of deposit consisting of a relatively loose, porous surface layer with a dense underlying film (Figs. 14 and 15). Distribution and analysis of the deposit

**TEST 2B PHASE III 5/24/66 - 6/9/66  
BOILERWATER CONDUCTIVITY**



**FRESHWATER ADDITIONS**



**TEST 2B PHASE III 5/24/66 - 6/9/66  
BOILERWATER pH**

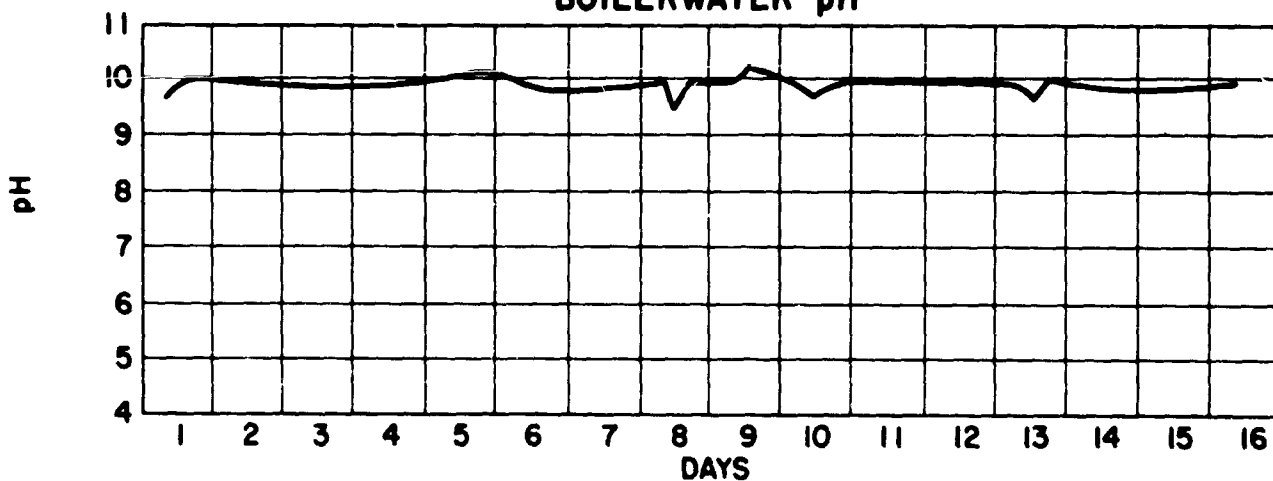


Fig. 7

**TEST 2B PHASE III  
PHOSPHATE WIDEOUT**

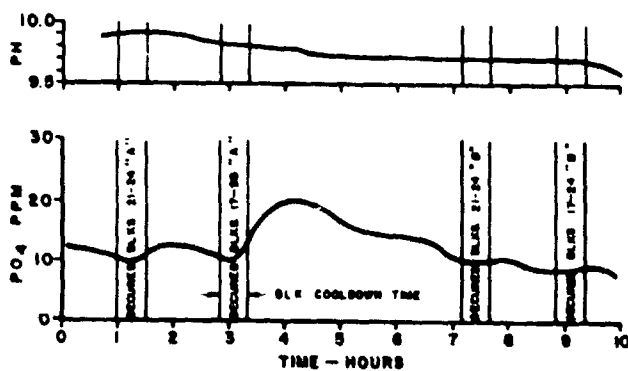


Fig. 8

removed from the test surfaces is shown by Table VII. The deposit was readily removed by soaking in the standard hydrochloric acid and thiourea solution, and the underlying metal was found to have experienced no measurable corrosion. Metallurgical examination revealed no changes in the metal structure.

**Log — Test 1C, Phase III**

Volatile ( $\text{NH}_3$ ) Boiler Water Treatment — pH = 8.6 to 9.0

'Dirty Boiler Conditions — Seawater Condenser Leakage

The surfaces of the loop were chemically cleaned with inhibited HCl, then passivated by alkaline boilout

**TABLE VI**  
**TEST 2B—PHASE III**  
**DEPOSIT DISTRIBUTION**

Loop	Q/A-Btu/hr-ft <sup>2</sup>	Heated/Unheated Side	Block Location	Gm/Linear Ft
A	150,000	Heated	20	1.033
A	150,000	Heated	19	0.832
A	150,000	Heated	17	0.543
A	—	Unheated	20	0.186
A	—	Unheated	19	0.252
A	—	Unheated	18	0.106
A	—	Unheated	17	0.144
B	150,000	Heated	20	0.587
B	150,000	Heated	19	0.689
B	150,000	Heated	17	0.475
B	—	Unheated	20	0.347
B	—	Unheated	19	0.451
B	—	Unheated	18	0.581
B	—	Unheated	17	0.396

**DEPOSIT ANALYSIS**

		A Loop	B Loop
X-Ray Diffraction	Major, > 30% Minor, 8 to 15% Trace, < 4%	Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> Cu, Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub> Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , Cu Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>
Spectrography	Major, > 15% Lo Major, 8 to 15% Minor, 3 to 8% Lo Minor, 1 to 3%	Fe Cu Ca Mg	Fe Cu Ca Mg
Chemical Analysis, %	SO <sub>3</sub> CO <sub>2</sub> P <sub>2</sub> O <sub>5</sub> SiO <sub>2</sub> Fe <sub>3</sub> O <sub>4</sub> CaO MgO Cu	Neg. Neg. 10 <1 65 7 2 14	Neg. Neg. 10 <1 68 6 2 11

**TABLE VII**  
**TEST 3B—PHASE III**  
**DEPOSIT DISTRIBUTION**

Loop	Q/A-Btu/hr-ft <sup>2</sup>	Heated/Unheated Side	Block Location	Gm/Linear Ft
A	150,000	Heated	20	0.4343
A	150,000	Heated	19	0.6583
A	150,000	Heated	18	0.8641
A	150,000	Heated	17	0.8528
A	—	Unheated	20	0.0196
A	—	Unheated	19	0.0278
A	—	Unheated	18	0.0444
A	—	Unheated	17	0.0323
B	150,000	Heated	20	0.7980
B	150,000	Heated	19	1.0686
B	150,000	Heated	18	1.0516
B	150,000	Heated	17	0.8505
B	—	Unheated	20	0.0112
B	—	Unheated	19	0.0382
B	—	Unheated	18	0.0362
B	—	Unheated	17	0.0427

		A Loop		B Loop	
		Heated Side	Unheated Side	Heated Side	Unheated Side
X-ray Diffraction	Major, 30% High Minor, 15 to 20% Minor, 8 to 15% Trace, < 4%	Fe <sub>2</sub> O <sub>3</sub> — — Fe <sub>3</sub> O <sub>4</sub> , Cu	Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub> Cu — Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , CaCO <sub>3</sub> SiO <sub>2</sub> (Quartz)	Fe <sub>2</sub> O <sub>3</sub> — — Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub> — Fe <sub>2</sub> O <sub>3</sub> , Cu —
(Analyses confirmed in two laboratories)					
Spectrography	Major, 15% Lo Major, 8 to 15% Minor, 3 to 8% Lo Minor, 1 to 3% Qualitative	Fe — — Cu, Si	Fe, Cu — Si, Ca Mg Slight PO <sub>4</sub> Trace CO <sub>3</sub>	Fe — — Cu, Si	Fe Cu Si Ni, Ca, Mg Trace PO <sub>4</sub>
Chemical Analysis, %	P <sub>2</sub> O <sub>5</sub> SiO <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub> Cu	3 1 93 1		4 — 93 1	



Fig. 9: Upper—Appearance of deposits formed on tube surfaces during Test 28  
Lower—Tube surface after removal of deposits by chemical cleaning

prior to starting this run. Subsequently the test sections were installed and the loop was placed in operation. Equilibrium hydrogen concentrations of 100 ppb were experienced shortly after start-up.

The initial introduction of seawater condenser leakage rapidly depressed the boiler pH to approximately 4.7 (Fig. 17). With the exception of a short duration increase in hydrogen evolution (Fig. 16) when the first introduction of iron oxide and copper was made, no increase in hydrogen concentration was observed throughout most of the first day's operation with depressed pH boiler water. The fourth injection of iron oxide and copper triggered a massive increase in hydrogen evolution which produced concentrations as high as 550 ppb. Approximately one hour after this excursion had begun the pH of the cooled boiler water sample was restored to specified limits by the introduction of ammonia. However, the addition of ammonia appeared to have no effect upon the rate of hydrogen evolution. Due to the high reflux condenser hydrogen



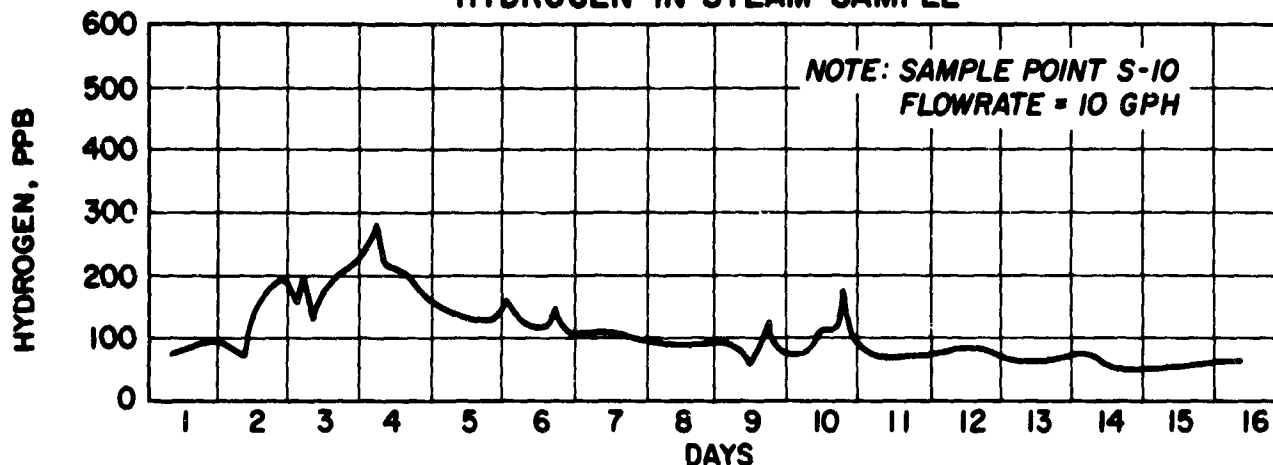
Fig. 10: 100X photomicrograph of the deposit cross section from Test 28

TABLE VIII  
TEST 1C—PHASE III  
WATER ANALYSIS

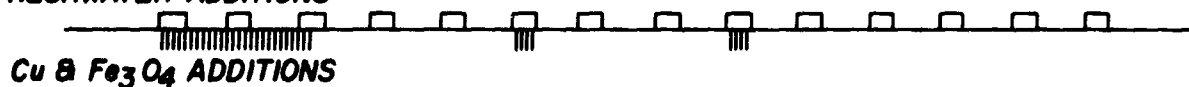
DATE	TIME	H <sub>2</sub> ppb	pH	Cond. μ mhos	Na ppm	Ca ppm	Mg ppm	Cl ppm	SO <sub>4</sub> ppm	Fe Total ppm	Cu Total ppm	SiO <sub>2</sub> ppm
8/9/66	0900	216	8.78	20	0.2	Trace	Neg.	0.6	—	—	—	0.202
	0930	BEGAN SEA WATER ADDITION										
	1000	154	8.38	66	8.8	0.4	0.5	14.8	—	0.008	0.040	0.226
	1100	290	7.13	155	24.3	0.4	2.2	46.5	—	—	—	0.240
	1200	564*	5.95	230	39.8	0.4	2.9	77.0	—	0.036	0.320	0.245
	1300	765*	5.50	265	48.0	0.8	2.9	81.8	1.4	—	—	0.284
	1400	900*	5.70	265	47.5	0.8	3.2	81.1	2.3	0.209	0.840	—
	1500	1059*	5.75	265	48.0	0.8	3.2	83.7	—	—	—	0.295
	1600	1116*	6.00	205	34.5	0.8	2.7	61.9	—	0.108	0.904	0.327
	1700	1128*	8.90	145	19.5	0.4	1.2	41.5	0.2	—	—	0.325
	1800	1143*	8.90	130	18.5	0.4	1.2	37.4	—	0.168	0.256	0.350
	1900	1095*	8.85	120	15.3	0.4	1.0	33.7	—	—	—	0.360
	2000	1077*	8.85	110	18.8	0.4	1.2	29.6	—	0.044	0.808	0.375
	2100	1026*	8.85	71	10.3	0.4	0.7	18.8	—	—	—	0.330
	2200	906*	8.80	51	6.8	0.4	0.2	7.3	—	0.036	0.368	0.310
	2300	750*	8.85	37	5.6	0.4	0.2	8.4	—	—	—	0.310
	2400	678*	8.95	33	4.8	0.4	0.2	8.0	—	0.012	0.048	0.310
	0100	482	9.00	28	4.0	0.4	0.2	5.8	—	—	—	0.290
	0200	424	8.95	18	2.0	0.4	0.2	2.6	—	0.104	0.944	0.289
	0300	336	8.92	15	1.5	0.0	0.2	3.4	0.6	—	—	0.300
	0400	276	8.90	13	1.2	0.0	0.2	2.6	—	0.012	0.088	0.310
	0500	223	9.10	13	1.0	0.0	0.2	2.2	—	—	—	—
	0600	205	8.80	10	0.8	0.0	0.2	1.9	—	0.020	0.128	—
	0700	177	8.90	8	0.6	0.0	0.0	1.4	—	—	—	0.310
	0800	191	8.90	8	0.5	0.0	0.0	1.5	—	0.240	0.112	0.340

\*Calculated reflux cond. hydrogen concentrations from drum steam samples

**TEST 3B PHASE III 6/5/66 - 6/20/66  
HYDROGEN IN STEAM SAMPLE**



**FRESHWATER ADDITIONS**



**TEST 3B PHASE III 6/5/66 - 6/20/66  
TEST CROWN TEMPERATURE RISE**

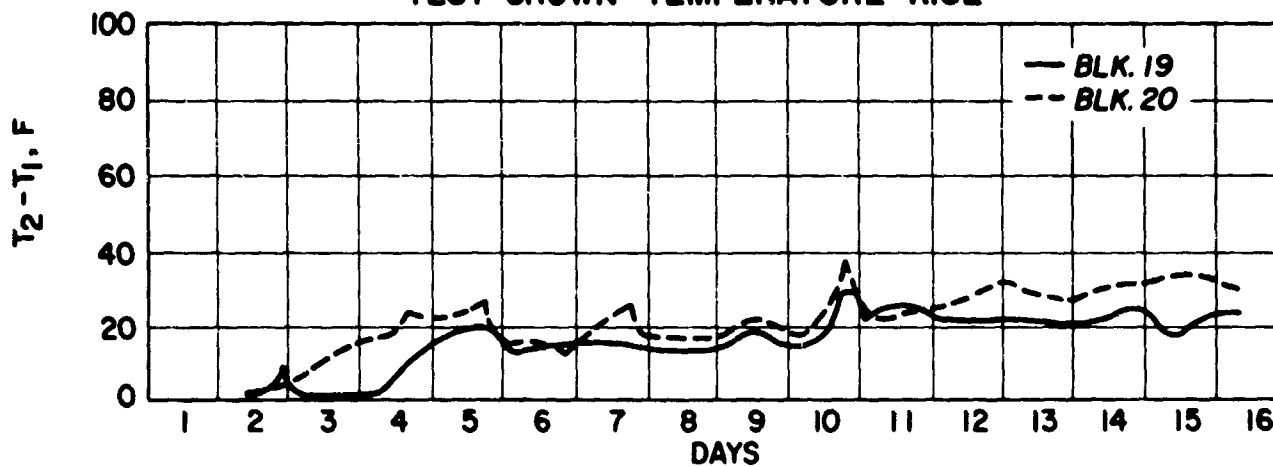


Fig. 11

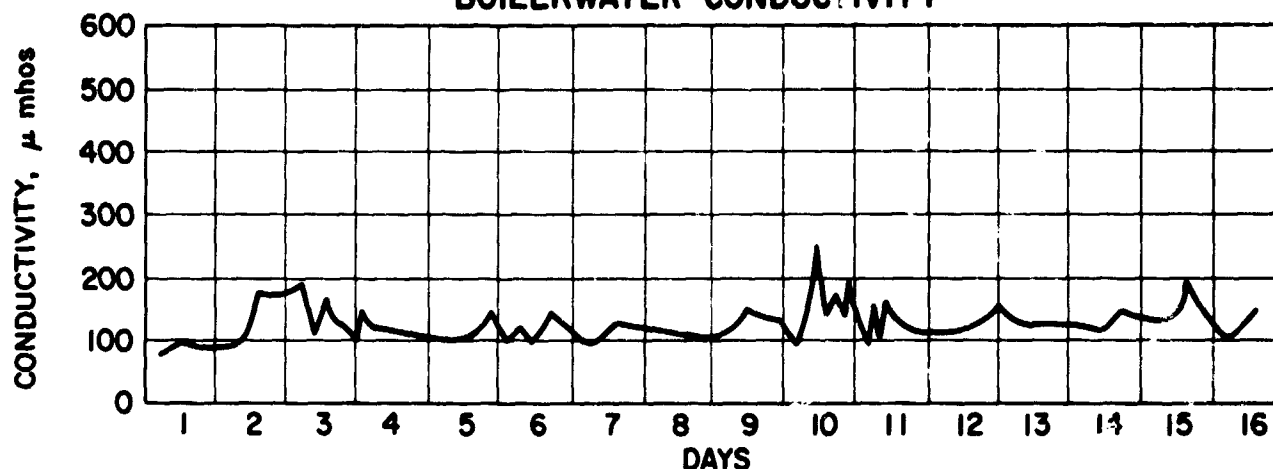
concentration and the rate of temperature increase noted at Block 19 A, only one additional injection of iron oxide and copper was made during this run (total added = 500 gr). As shown by Figs. 16 and 17, hydrogen concentrations increased in spite of re-establishing the pH. Boiler water conductivity was reduced by blowdown for approximately 8 hours before a reduction in hydrogen evolution was noted. Hydrogen concentrations decreased to approximately 150 ppb during the night.

No further additions of iron oxide and copper were made on the second day of testing; however, seawater condenser leakage was added throughout the day shift. An immediate depression in pH resulted from the initial

injections of seawater. Hydrogen concentrations began to rise immediately upon depression of pH, exceeding the full scale reading of the hydrogen analyzer for approximately a 13-hour period. During the second day of operation, no significant reduction in hydrogen evolution was experienced until the boiler water solids were reduced by blowdown. After this massive hydrogen excursion, it was found that the Block 19 A tube crown temperature had increased approximately 45 F. No appreciable rise in temperature was noted at any other location.

Based upon the hydrogen evolved during these two days of operation and the accompanying rapid rise in tube crown temperature, it appeared that extensive

### TEST 3B PHASE III 6/5/66 - 6/20/66 BOILERWATER CONDUCTIVITY



#### FRESHWATER ADDITIONS



### TEST 3B PHASE III 6/5/66 - 6/20/66 BOILERWATER pH

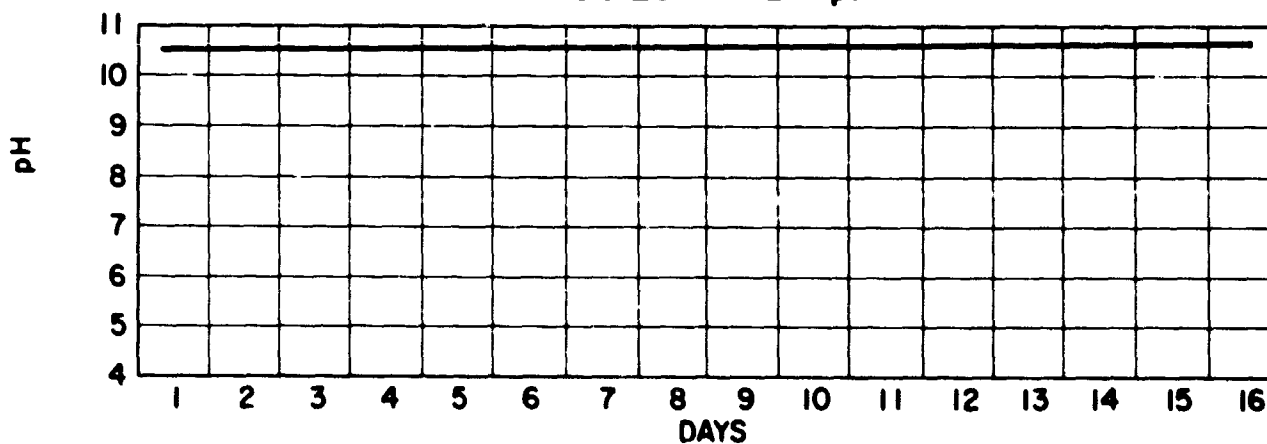


Fig. 12

#### TEST 3B PHASE III PHOSPHATE WIDEOUT

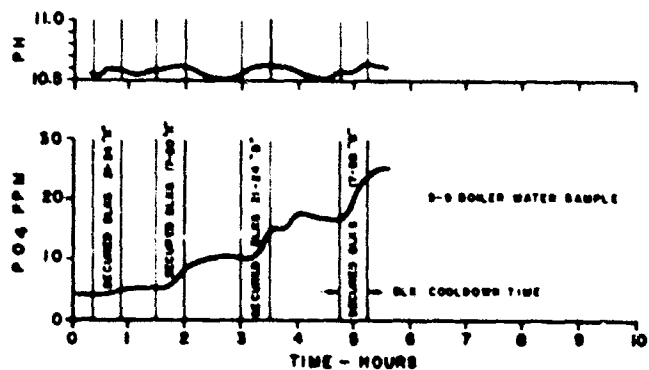


Fig. 13

corrosion had occurred at the Block 19A location. On this basis, it was decided: first, to decrease the heat flux late in the afternoon of the second day of operation, and second, to terminate the test once the hydrogen concentrations had been restored to normal level. Shutdown was initiated at approximately noon on the third day of testing. Throughout the period of the excursion and the restoration of loop conditions to normal, hourly boiler water and millipore filter samples were taken. Results of the analyses of these samples are included in Table VIII and IX.

Inspection of the test sections revealed that corrosion was not restricted to the Block 19 location. Corrosion sites were found throughout both the high and low

TABLE IX  
TEST 1C—PHASE III

X-RAY DIFFRACTION ANALYSIS OF MATERIAL FILTERED\* FROM BW

Date	Time	Major	Minor	Trace	Possible
8/9/66	1030	Cu <sub>2</sub> O	Mg(OH) <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub> , Cu	—
	1135	Mg(OH) <sub>2</sub>	Cu <sub>2</sub> O	Cu, Fe <sub>3</sub> O <sub>4</sub>	—
	1200	Cu <sub>2</sub> O	Mg(OH) <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub> , Cu	—
	1300	Cu <sub>2</sub> O	Mg(OH) <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub> , Cu	—
	1400	Cu <sub>2</sub> O	Mg(OH) <sub>2</sub> , Cu	Fe <sub>3</sub> O <sub>4</sub>	—
	1500	Cu <sub>2</sub> O, Mg(OH) <sub>2</sub>	—	Fe <sub>3</sub> O <sub>4</sub> , Cu	—
	1700	Mg(OH) <sub>2</sub>	CuO	Cu, Fe <sub>3</sub> O <sub>4</sub> , Cu <sub>2</sub> O	—
	1800	Mg(OH) <sub>2</sub>	Cu <sub>2</sub> O, Fe <sub>3</sub> O <sub>4</sub>	Cu	—
	1900	Cu <sub>2</sub> O, Mg(OH) <sub>2</sub>	—	Fe <sub>3</sub> O <sub>4</sub> , Cu	—
	2000	Cu <sub>2</sub> O, Mg(OH) <sub>2</sub> , Fe <sub>3</sub> O <sub>4</sub>	—	Cu	—
	2100	Mg(OH) <sub>2</sub>	Cu <sub>2</sub> O	Fe <sub>3</sub> O <sub>4</sub> , Cu	—
	2300	Mg(OH) <sub>2</sub>	—	Cu <sub>2</sub> O, Fe <sub>3</sub> O <sub>4</sub> , Cu	—
8/10/66	0200	Mg(OH) <sub>2</sub>	—	Cu <sub>2</sub> O, Fe <sub>3</sub> O <sub>4</sub> , Cu	—
	0400	Mg(OH) <sub>2</sub>	—	Cu <sub>2</sub> O	Fe <sub>3</sub> O <sub>4</sub> , Cu
	0600	Mg(OH) <sub>2</sub>	—	Fe <sub>3</sub> O <sub>4</sub>	Cu <sub>2</sub> O, Cu
	0800	Mg(OH) <sub>2</sub>	—	Cu <sub>2</sub> O, Fe <sub>3</sub> O <sub>4</sub> , Cu	2(Mg·9Fe·1)OSiO <sub>2</sub> 2(Mg·9Fe·1)OSiO <sub>2</sub>

\*0.45 micron pore size

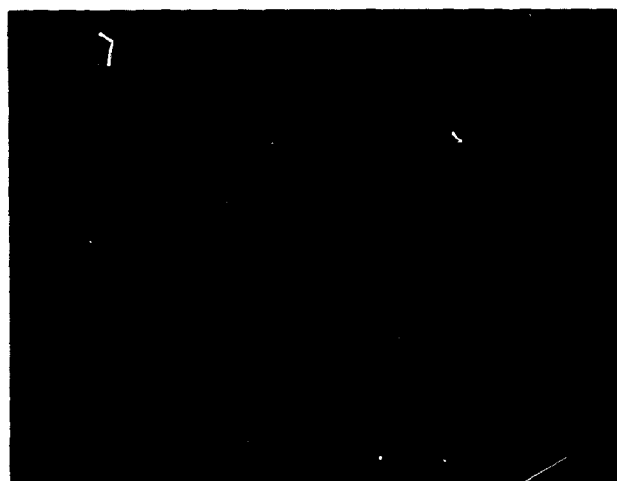


Fig. 14: Upper—Appearance of deposits formed on tube surfaces during Test 38  
Lower—Tube surface after removal of deposits by chemical cleaning

heat-flux zones of the "A" and "B" test loops. Inspection of the metal surfaces revealed that corrosion sites were covered with a dense brittle oxide (25-mils thick) and that uncorroded areas were covered with a thinner less dense material (Figs. 18 and 19). Deposit distribution and analyses are included in Table X. Specimens from the test sections were removed and chemically cleaned using the standard hydrochloric acid, ammonium bifluoride, and thiourea solution. The deposits were difficult to remove, requiring several hours soaking in the solution and considerable agitation. The underlying metal revealed that penetration had occurred to a depth of approximately 5 to 6 mils in random plugs approximately the size of a half dollar. The surface of the metal at the areas of attack appeared to have an etched appearance while the uncorroded portions of the heated and unheated tubing appeared normal. Metallurgical examinations of the corroded specimens showed that no changes had occurred in the metal structure.



Fig. 15: 100X photomicrograph of the deposit cross section from Test 38



TABLE X  
TEST 1C—PHASE III

DEPOSIT DISTRIBUTION				
Loop	Q/A-Btu/hr-ft <sup>2</sup>	Heated/Unheated Side	Block Location	Gm/Linear Ft
A	150,000	Heated	18	2.6628
A	150,000	Heated	17	3.1752
B	150,000	Heated	20	2.4959
B	150,000	Heated	19	0.4857
B	150,000	Heated	18	0.0798
B	150,000	Heated	17	0.0380
A & B	—	Unheated	17-20	~0.01

DEPOSIT ANALYSIS

		A Loop		B Loop		A and B Loop Unheated Side
		Corroded Area	Uncorroded Area	Corroded Area	Uncorroded Area	
X-ray Diffraction	Major, >30%	Fe <sub>3</sub> O <sub>4</sub>	Mg(OH) <sub>2</sub> Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>	Mg(OH) <sub>2</sub> Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>
	Minor, 8 to 15%	—	CaSO <sub>4</sub> 3MgO·2SiO <sub>2</sub> ·2H <sub>2</sub> O (Serpentine)	—	—	—
	Lo Minor, 4 to 8%	Mg(OH) <sub>2</sub>	—	Mg(OH) <sub>2</sub>	3MgO·2SiO <sub>2</sub> ·2H <sub>2</sub> O (Serpentine) CaSO <sub>4</sub>	—
	Trace, <4%	—	—	—	Fe <sub>2</sub> O <sub>3</sub>	—
Spectrography	Major, >15%	Fe	Mg, Fe	Fe	Fe, Mg	Fe
	Minor, 3 to 8%	Mg	Si, Ca	Mg	Si	—
	Lo Minor, 1 to 3%	Cu, Si	—	Si, Cu	Ca, Cu	Cu, Si, Mg
	Qualitative	—	Slight SO <sub>4</sub>	—	—	—
Chemical Analysis, %	SiO <sub>2</sub>	1	5	1	Insufficient Sample	
	Fe <sub>3</sub> O <sub>4</sub>	88	32	91		
	CaO	1	6	—		
	MgO	4	33	5		
	Cu	3	—	1		
	SO <sub>3</sub>	Neg.	7	Neg.		
	CO <sub>2</sub>	Neg.	Neg.	Neg.		
	P <sub>2</sub> O <sub>5</sub>	<1	<1	<1		

TABLE XI  
TEST 2C—PHASE III

WATER ANALYSIS													
DATE	TIME	H <sub>2</sub> ppb	pH	Cond. μ mhos	Na ppm	Ca ppm	Mg ppm	PO <sub>4</sub> ppm	Cl ppm	SO <sub>4</sub> ppm	Fe Total ppm	Cu Total ppm	SiO <sub>2</sub> ppm
9/20/66	0900	51	10.0	52	6	0	0	7	3	0	0.020	0.122	0.560
	1000	57	9.6	68	9	0	0	3	13	2	—	—	0.403
	1100	48	5.7	140	20	0	0	1	35	3	—	—	0.112
	1200	51	4.7	192	37	0	0.2	0	60	—	0.180	0.550	0.079
	1300	53	4.7	198	34	0	0	0	54	—	—	—	0.068
	1400	63	4.8	192	30	0	0	0	51	—	—	—	0.064
	1500	84	4.9	176	25	0	0	0	43	—	0.124	0.490	0.064
	1600	102	4.8	152	—	0	0	0	—	—	—	—	0.084
	1700	189	8.8	200	—	0	0	8	—	—	—	—	—
	1800	231	9.3	180	21	0	0	10	21	—	0.090	0.068	0.140
	1900	100	10.0	175	21	0	0	11	26	—	—	—	0.104
	2000	62	9.9	150	18	0	0	10	22	—	—	—	0.108
	2100	60	9.9	130	15	0	0	9	19	—	0.060	0.002	0.610
	2200	52	10.0	115	12	0	0	10	14	—	—	—	0.562
	2300	51	10.0	90	10	0	—	10	8	—	—	—	0.350
	2400	51	10.0	75	8	0	0	9	6	—	—	—	0.723

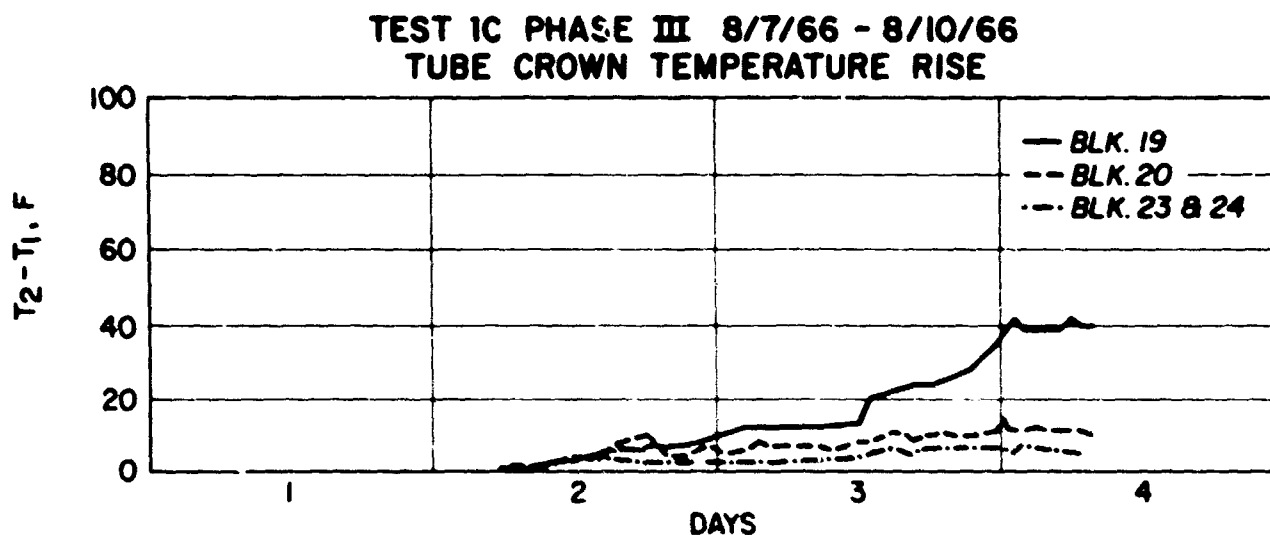
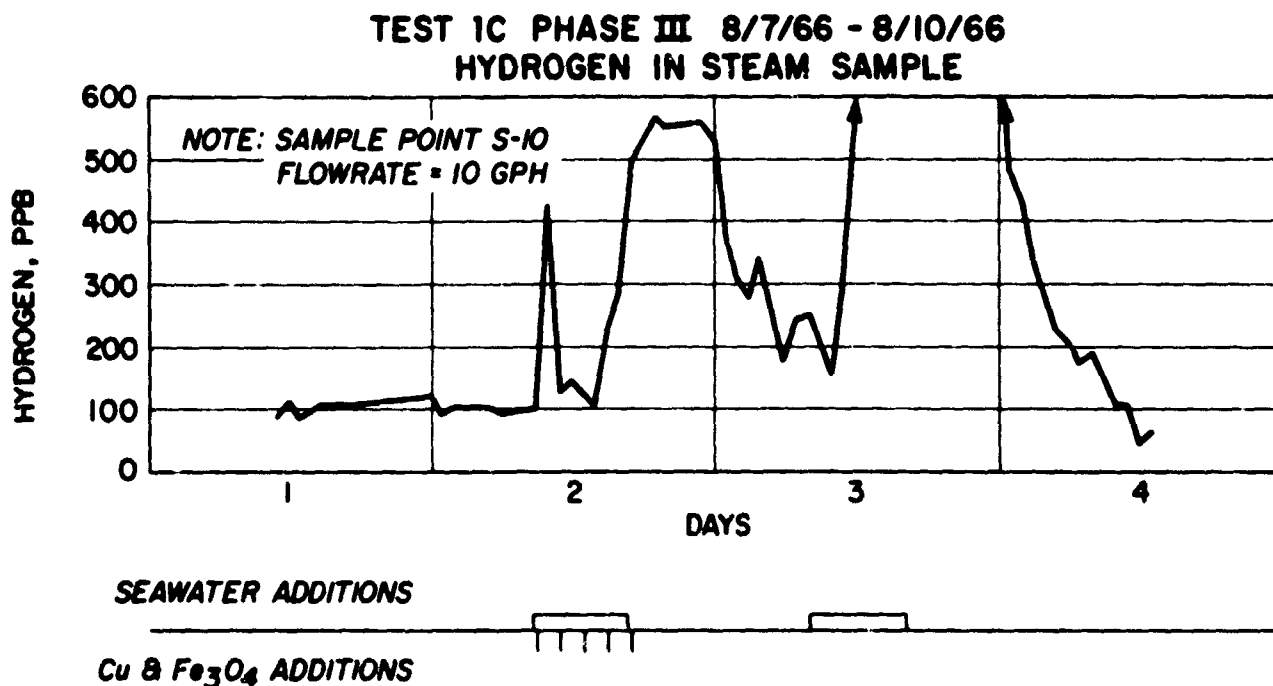


Fig. 16

**Log — Test 2C, Phase III**

Coordinated Phosphate Boiler Water Treatment  
— pH = 9.8 to 10.0

Dirty Boiler Conditions Seawater Condenser  
Leakage

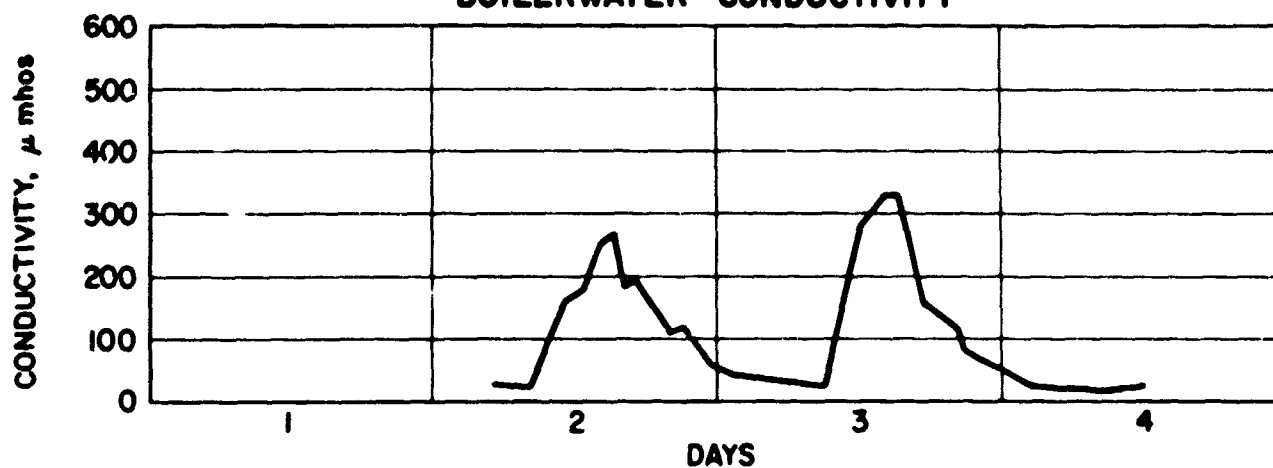
An equilibrium base hydrogen concentration of approximately 100 ppb was established shortly after start-up (Fig. 20). On the following day seawater contaminant addition was begun; however, the introduction of copper and iron oxide was delayed so that the effects of condenser leakage could be observed without other contaminants present. In spite of a depression in pH to approximately 5.0, no increase in hydrogen evolution

was noted. Iron oxide and copper additions were begun on the third operating day and subsequently pH excursions were accompanied by excursions in hydrogen evolution. The effect of seawater introduction on pH and conductivity may be seen in Fig. 21.

Seawater injection was stopped on the thirteenth day of operation since the tube crown temperatures at all test locations had increased to high values. Block 20A experienced the greatest temperature rise, approximately 100 F. Hydrogen concentrations remained at approximately 50 ppb for the last several days of operation with no additions of seawater contaminants.

Table XI shows typical analyses of the boiler water during a period of condenser leakage, defining the range

**TEST 1C PHASE III 8/7/66 - 8/10/66  
BOILERWATER CONDUCTIVITY**



**SEAWATER ADDITIONS**



**TEST 1C PHASE III 8/7/66 - 8/10/66  
BOILERWATER pH**

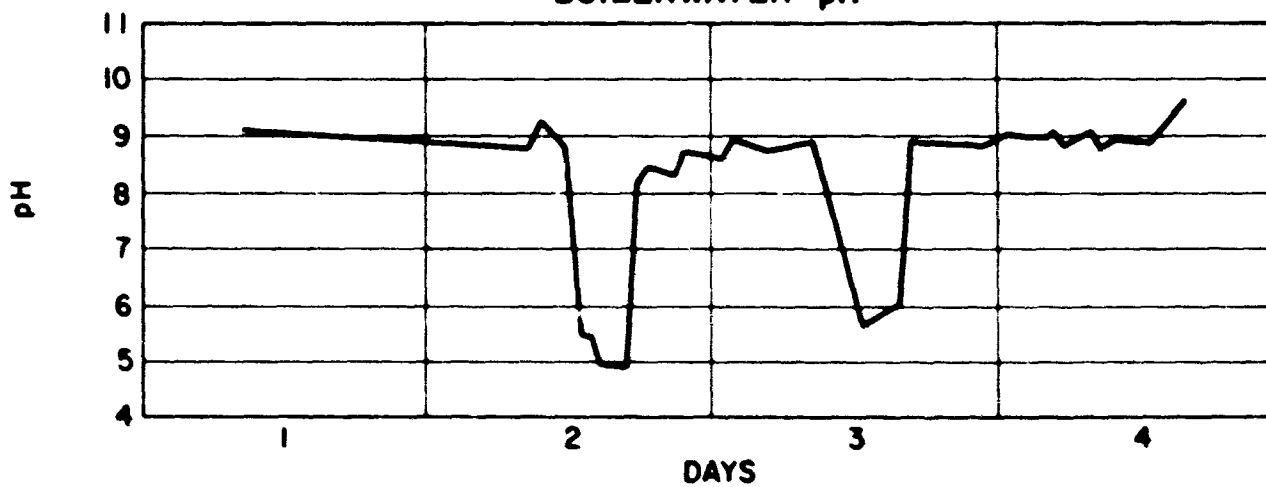


Fig. 17

**TABLE XH  
TEST 2C-PHASE III**

**X-RAY DIFFRACTION ANALYSIS OF MATERIAL FILTERED FROM BW**

Date	Time	Major	Minor	Trace	Possible
9/20/66	0700	Cu	Cu <sub>2</sub> O, Fe <sub>2</sub> O <sub>3</sub>	—	—
	0900	No Lines			
	1000				
	1100				
	1200				
	1300				
	1400	Fe <sub>2</sub> O <sub>3</sub>	—	—	—
	1500	Fe <sub>2</sub> O <sub>3</sub>	—	—	—
	1600	No Lines			
	1700	Cu <sub>2</sub> O	—	Cu, Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
	1800	Cu <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	Cu	Fe <sub>2</sub> O <sub>3</sub>
	1900	Fe <sub>2</sub> O <sub>3</sub>	Cu	Cu <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>
	2100	Cu	Fe <sub>2</sub> O <sub>3</sub> , Cu <sub>2</sub> O	—	—
	2200	Cu, Fe <sub>2</sub> O <sub>3</sub>	—	—	—
	2300	Fe <sub>2</sub> O <sub>3</sub>	Cu	Cu <sub>2</sub> O	—

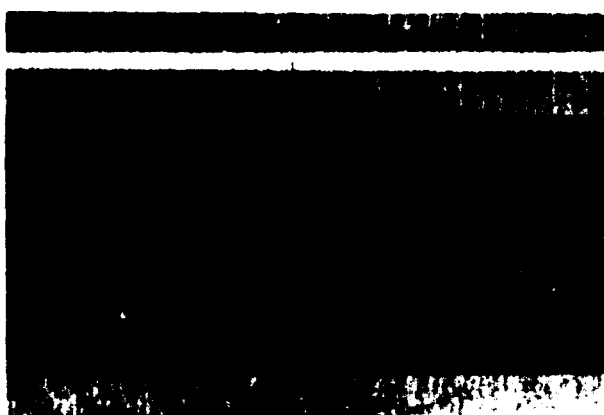


Fig. 18: Upper—Appearance of deposits formed on tube surfaces and corrosion "plugs" from Test 1C

Lower—Tube surface after removal of deposits by chemical cleaning



Fig. 19 100X photomicrograph of the deposit cross section from Test 1C

of chemistry from the time prior to the introduction of contaminants, through a pH-hydrogen excursion, and the period when control conditions were re-established. Analyses of millipore filter residues are also included (Table XII). During shutdown of the loop phosphate concentrations increased as shown by Fig. 22. Examination of the test sections revealed that the internal surfaces were covered with a dense deposit approximately 40 mils thick (Figs. 23 and 24). The distribution and composition of deposits are shown in Table XIII.

Deposits were removed from specimens with great difficulty by chemical and mechanical cleaning, and the underlying metal was examined. Considerable surface pitting to a depth of approximately 5 mils was noted. This random attack was observed throughout most of the heated surfaces.

Initial metallurgical examination revealed some surface decarburization in localized areas. In order to ascertain the significance of the decarburization, it was decided to examine the ductility of the material. It was felt that such a test would indicate whether or not incipient hydrogen damage was present. Tensile test specimens were prepared from sections of the heated and unheated sides of the tubing. The specimens were pulled to failure and sections were removed for metallurgical examination. As shown by Fig. 25, no fissuring was present nor loss of ductility experienced.

#### Log Test 3C, Phase III

Free Caustic Boiler Water Treatment pH = 10.5 to 10.7

Dirty Boiler Conditions Seawater Condenser Leakage

A base hydrogen concentration of approximately 100 ppb was established shortly after startup and seawater addition was begun. Copper and iron oxide injections were delayed for an additional day. As shown in Figs. 26 and 27, the introduction of seawater condenser leakage depressed the pH during each of the first 12 days of operation. No increases in hydrogen concentration occurred with low pH operation until after the injection of preboiler corrosion products. Excursions in pH generally resulted in increases in hydrogen evolution; however, on the last three days of operation neither significant changes in pH nor hydrogen concentration were noted. During this period the increase in conductivity was the same as had been experienced with previous additions of seawater.

Table XIV illustrates typical variations in boiler water chemistry during a pH-hydrogen excursion

TABLE XIII  
TEST 2C—PHASE III

DEPOSIT DISTRIBUTION				
Loop	Q/A-Btu/hr-ft <sup>2</sup>	Heated/Unheated Side	Block Location	Gm/Linear Ft
A	150,000	Heated	20	5.5755
A	150,000	Heated	19	7.3672
A	150,000	Heated	18	3.3642
A	150,000	Heated	17	1.8360
A	—	Unheated	20	0.0167
A	—	Unheated	19	0.0187
A	—	Unheated	18	0.0099
A	—	Unheated	17	0.0313
B	150,000	Heated	20	0.7143
B	150,000	Heated	19	0.6903
B	150,000	Heated	18	0.5172
B	150,000	Heated	17	1.399
B	—	Unheated	20	0.0811
B	—	Unheated	19	0.0325
B	—	Unheated	18	0.0487
B	—	Unheated	17	0.0982

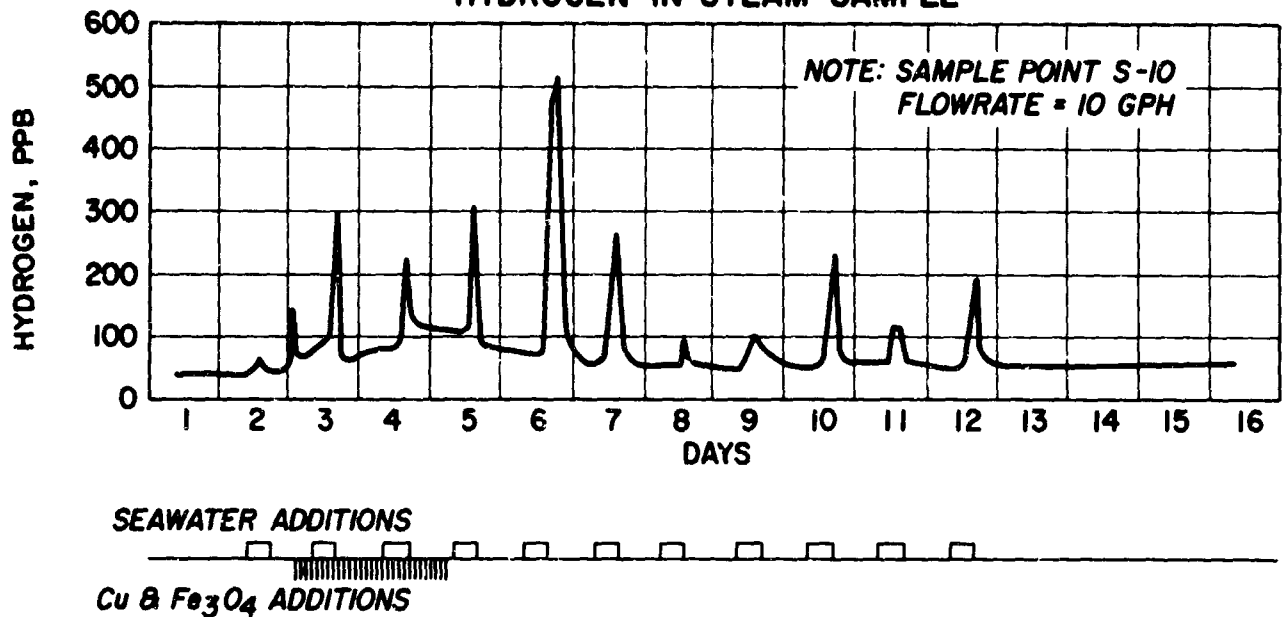
DEPOSIT ANALYSIS

		A Loop Heated Side	B Loop Heated Side	B Loop Unheated Side
X-ray Diffraction	Major, 30%	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Cu
	Hi Minor, 15 to 20%	—	—	Fe <sub>2</sub> O <sub>3</sub>
	Lo Minor, 4 to 8%	—	Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub> Cu	—
Spectrography	Trace, <4%	Fe <sub>2</sub> O <sub>3</sub> , CaCO <sub>3</sub>	—	—
	Major, 15%	Fe	Fe	Cu, Fe
	Minor, 3 to 8%	Na	Mg, Ca, Cu, Na	—
	Lo Minor, 1 to 3%	Mg, Ca, Cu	Si	Mg, Si, Ca
	Qualitative	Considerable PO <sub>4</sub> Trace CO <sub>2</sub>	Considerable PO <sub>4</sub> Trace SO <sub>4</sub> Trace CO <sub>2</sub>	Slight PO <sub>4</sub>
Chemical Analysis, %	SO <sub>2</sub>	—	1	—
	P <sub>2</sub> O <sub>5</sub>	29	18	3
	SiO <sub>2</sub>	1	1	2
	Fe <sub>2</sub> O <sub>3</sub>	56	65	21
	CaO	1	3	2
	MgO	2	5	3
	NaO	12	6	—
	Cu	2	3	70

TABLE XIV  
TEST 3C—PHASE III

WATER ANALYSIS														
DATE	TIME	H <sub>2</sub> ppm	pH	Cond. μ mhos	Na ppm	Ca ppm	Mg ppm	OH ppm	PO <sub>4</sub> ppm	Cl ppm	SO <sub>4</sub> ppm	Fe ppm	Cu ppm	SiO <sub>2</sub> ppm
10/26/66	0800	219	10.6	110	—	—	—	—	2.3	—	—	—	—	0.024
	0900	225	10.6	120	—	—	—	—	1.5	—	—	—	—	0.025
	1000	186	10.4	105	12	0	0	3.23	0.4	10	—	0.046	0.012	—
	1100	144	10.1	150	21	0	0	1.19	0	26	5	—	—	0.030
	1200	108	9.5	185	30	0	0	—	0	36	—	0.004	0.011	—
	1300	87	8.4	265	44	0	0	2.38	0	52	8	—	—	0.054
	1400	72	5.5	320	52	0	0	0	0	68	—	0.027	0.112	—
	1500	72	4.6	395	70	0	0	0	0	82	14	—	—	0.104
	1600	300	4.5	430	76	0	0.2	0	0	82	—	0.101	0.106	—
	1700	365	5.2	350	56	0	0	0	0.4	76	10	—	—	0.074
	1800	513	10.2	260	44	0	0	4.08	0.6	40	—	0.032	0.017	—
	1900	280	10.6	230	36	0	0	5.61	1.0	30	8	—	—	0.038
	2000	194	10.6	215	36	0	0	5.27	1.0	30	—	0.005	0.012	—
	2100	194	10.8	215	37	0	0	6.3	1.0	27	5	—	—	0.046
	2200	204	10.6	185	29	0	0	4.8	0.6	21	—	0.003	0.011	—
	2300	190	10.5	150	22	0	0	3.2	2.2	16	7	—	—	0.104
	2400	210	10.7	165	30	0	0	9.7	2.2	16	—	0.001	0.012	—
10/27/66	0100	336	10.7	200	20	0	0	6.3	2.2	12	5	—	—	0.104
	0200	307	10.7	160	15	0	0	4.6	1.0	9	—	0.003	0.015	—

### TEST 2C PHASE III 9/11/66 - 9/26/66 HYDROGEN IN STEAM SAMPLE



### TEST 2C PHASE III 9/11/66 - 9/26/66 TUBE CROWN TEMPERATURE RISE

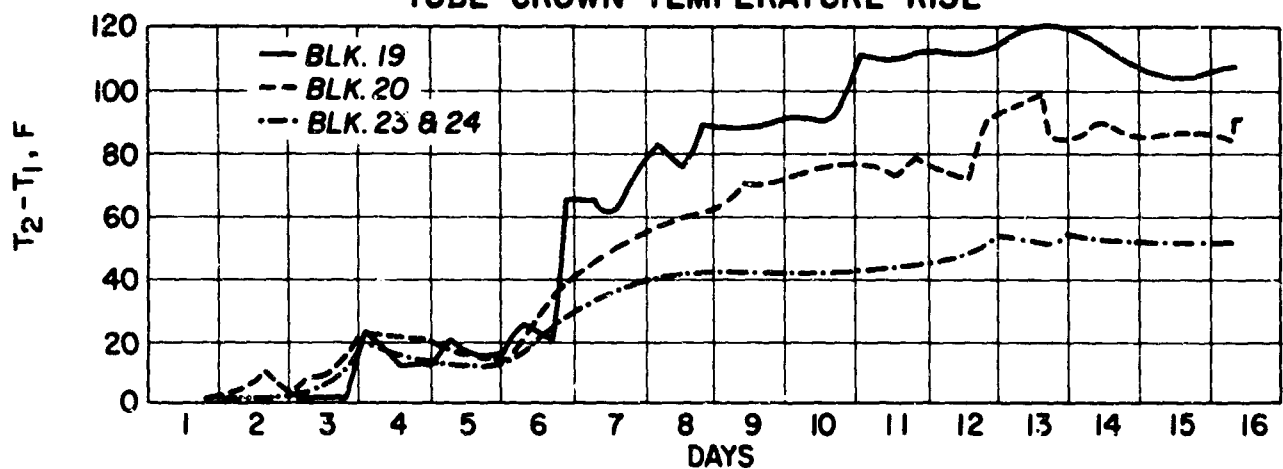


Fig. 20

resulting from seawater injection. Also included (Table XV) are analyses of millipore filter residues accumulated during the same operating period. Figure 28 shows the phosphate hideout data obtained during shutdown. A maximum tube crown increase of 30 F was experienced at Block 20A.

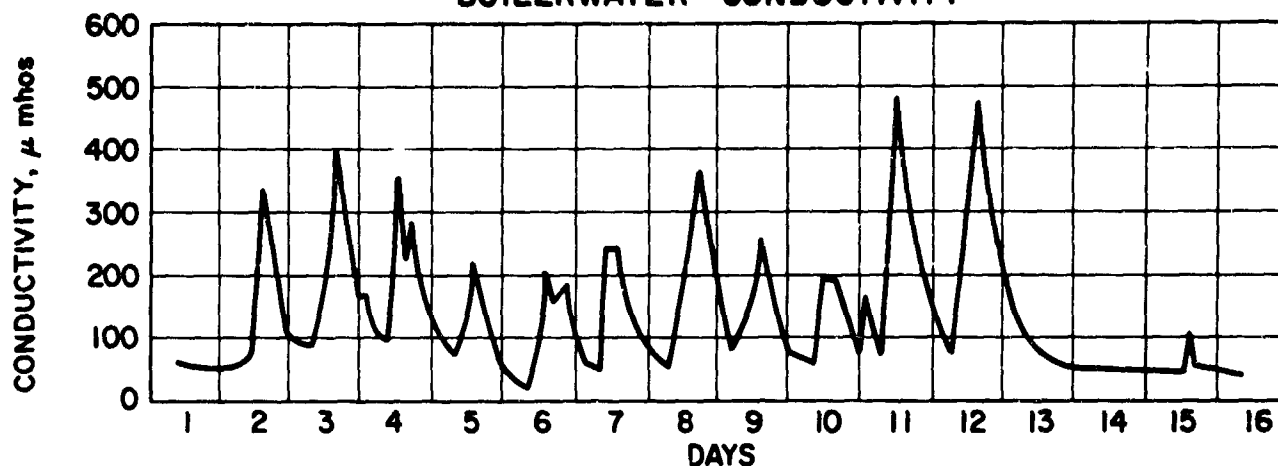
Examination of test sections revealed that the internal surfaces were covered with a relatively porous deposit approximately 45 mils thick (Figs. 29 and 30). Distribution and analysis of the deposits are listed in Table XVI. The deposits were removed from the test surfaces by chemical cleaning with the standard hydrochloric acid, ammonium bifluoride, and thiourea solution, and the surface inspected. Examination revealed

considerable attack in various areas (Fig. 29). Corrosion sites were similar in appearance, but smaller than the plugs seen after test 1C. The depth of corrosion was estimated to be approximately 10 mils maximum penetration. Metallurgical examination revealed no changes in metal structure.

#### DISCUSSION OF RESULTS

The discussion of results is divided into two sections each of which includes observations from the six tests of Phase III, Groups B and C, as well as comparisons with the previously reported results of the Phase III, Group A tests. The two subjects discussed in these sections are (1) deposits and (2) corrosion.

**TEST 2C PHASE III 9/11/66 - 9/26/66  
BOILERWATER CONDUCTIVITY**



**SEAWATER ADDITIONS**



**TEST 2C PHASE III 9/11/66 - 9/26/66  
BOILERWATER pH**

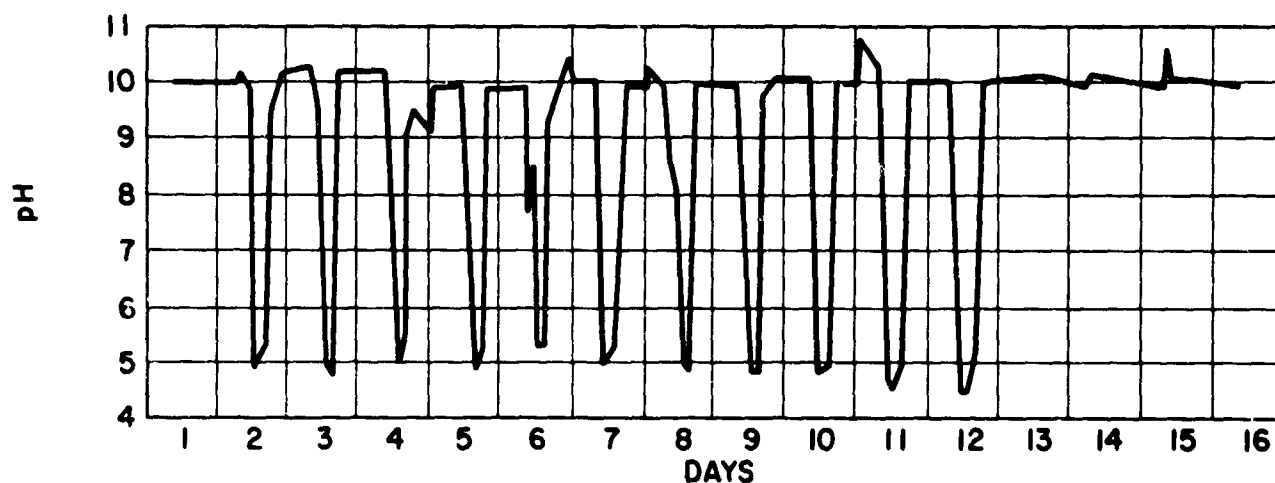


Fig. 21

**TABLE XV  
TEST 3C—PHASE III**

**X-RAY DIFFRACTION ANALYSIS OF MATERIAL FILTERED FROM BW**

Date	Time	Major	Minor	Trace	Possible
10/26/66	0900	No Residue on Filter			
	1000				
	1100	Fe <sub>3</sub> O <sub>4</sub>	—	—	—
	1200	Fe <sub>3</sub> O <sub>4</sub>	—	—	3 faint lines unidentified
	1300	Fe <sub>3</sub> O <sub>4</sub>	Cu <sub>2</sub> O	—	—
	1400	Fe <sub>3</sub> O <sub>4</sub>	—	—	3 faint lines unidentified
	1500	—	—	—	—
	1600	Fe <sub>3</sub> O <sub>4</sub>	—	—	—
	1700	Fe <sub>3</sub> O <sub>4</sub>	—	—	—
	1800	No Residue on Filter			
	1900	Cu	Cu <sub>2</sub> O	—	—
	2000	Fe <sub>3</sub> O <sub>4</sub>	Cu <sub>2</sub> O	Cu	3 faint lines unidentified
	2200	Fe <sub>3</sub> O <sub>4</sub>	—	—	—

TABLE XVI  
TEST 3C—PHASE III

DEPOSIT DISTRIBUTION				
Loop	Q/A-Btu/hr-ft <sup>2</sup>	Heated/Unheated Side	Block Location	Gm/Linear Ft
A	150,000	Heated	20	4.5867
A	150,000	Heated	19	1.4889
A	150,000	Heated	18	1.7067
A	150,000	Heated	17	2.7601
A	—	Unheated	20	0.2329
A	—	Unheated	19	0.1725
A	—	Unheated	18	0.2258
A	—	Unheated	17	0.2815
B	150,000	Heated	20	2.0319
B	150,000	Heated	19	1.4352
B	150,000	Heated	18	2.7256
B	150,000	Heated	17	2.3906
B	—	Unheated	20	0.1673
B	—	Unheated	19	0.1774
B	—	Unheated	18	0.0935
B	—	Unheated	17	0.1020

#### DEPOSIT ANALYSIS

		A Loop		B Loop	
		Heated Side	Unheated Side	Heated Side	Unheated Side
X-ray Diffraction	Major, 30%	Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>	Cu
	Minor, 15 to 20%	—	Cu	Cu	Cu <sub>2</sub> O, Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub>
	Lo Minor, 4 to 8%	Cu	Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	—
	Trace, <4%	—	Fe <sub>2</sub> O <sub>3</sub>	—	—
Spectrography	Major, 15%	Fe	Fe	Fe	Cu, Fe
	Lo Major, 8 to 15%	—	Cu	Cu, Mg	—
	Minor, 3 to 8%	Cu	Mg	Ca	—
	Lo Minor, 1 to 3%	Mg, Ca, Si	Ca, Si	Si, Na	—
Chemical Analysis, %	SO <sub>3</sub>	Neg.	Neg.	Neg.	—
	CO <sub>2</sub>	Neg.	—	—	—
	P <sub>2</sub> O <sub>5</sub>	5	5	10	—
	SiO <sub>2</sub>	1	1	1	—
	Fe <sub>2</sub> O <sub>3</sub>	—	—	—	27
	Fe <sub>3</sub> O <sub>4</sub>	84	90	71	—
	CaO	2	2	3	—
	MgO	3	4	7	—
	Cu	7	10	10	68

TEST 2C PHASE III  
PHOSPHATE HIDEOUT

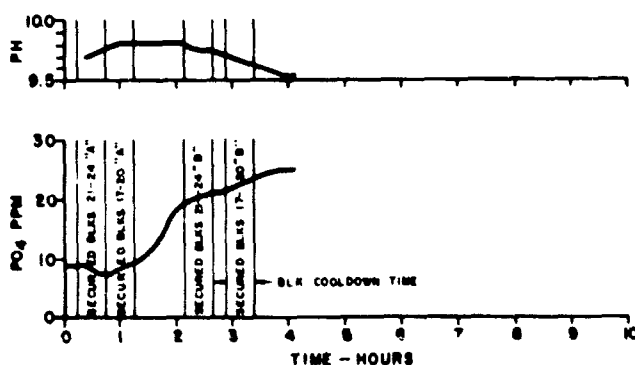
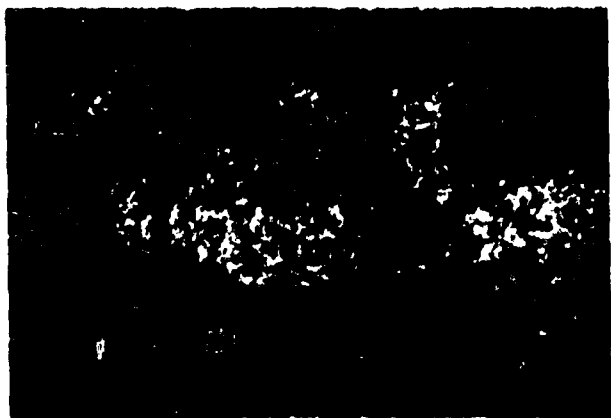


Fig. 22

#### Deposits

The second progress report on "A Research Study of Internal Corrosion of High Pressure Boilers," described some observed trends in the deposition of corrosion products and their relationship to local heat flux and mixture quality. The results of the last six tests, during which condenser leakage as well as corrosion products were injected, reveal some differences in the distribution of deposits on heat transfer surfaces from those previously reported. In general, during both groups of tests, the deposition of contaminants was greater at the high heat flux than in the lower heat-flux locations; however, quality did not appear to have a pronounced effect during tests with condenser leakage.





*Fig. 23: Upper—Appearance of deposits formed on tube surface during Test 2C*

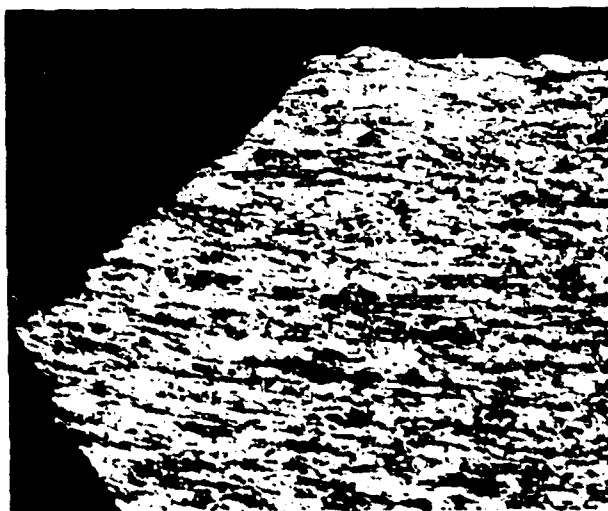
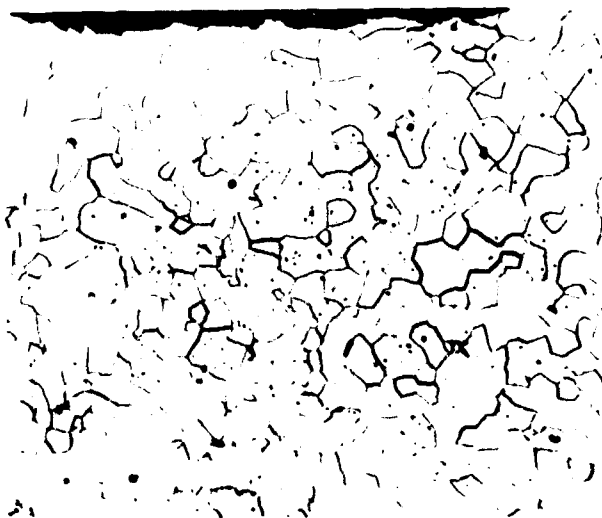
*Lower—Tube surface after removal of deposits by chemical cleaning*

The weight of deposits found on the tube surfaces from the volatile and coordinated phosphate tests, with fresh water condenser leakage, did not vary significantly from the corresponding tests during which only simulated preboiler corrosion products were employed. However, the presence of precipitated salts resulted in the formation of slightly thicker, less dense deposits which induced greater increases in tube metal temperature (20 to 27 F vs 0 to 7 F).

The results of the free-caustic-treatment, fresh-water condenser-leakage test were vastly different from those of the previous caustic test during which heavy deposits of iron oxide and copper accumulated and severe corrosion occurred. Neither additions of iron oxide and copper nor injections of fresh-water condenser leakage produced elevations in tube-metal temperature comparable to the earlier test. The small increases in temperature which resulted from additions of corrosion products were short lived in contrast to the longer duration cycles previously experienced. These data



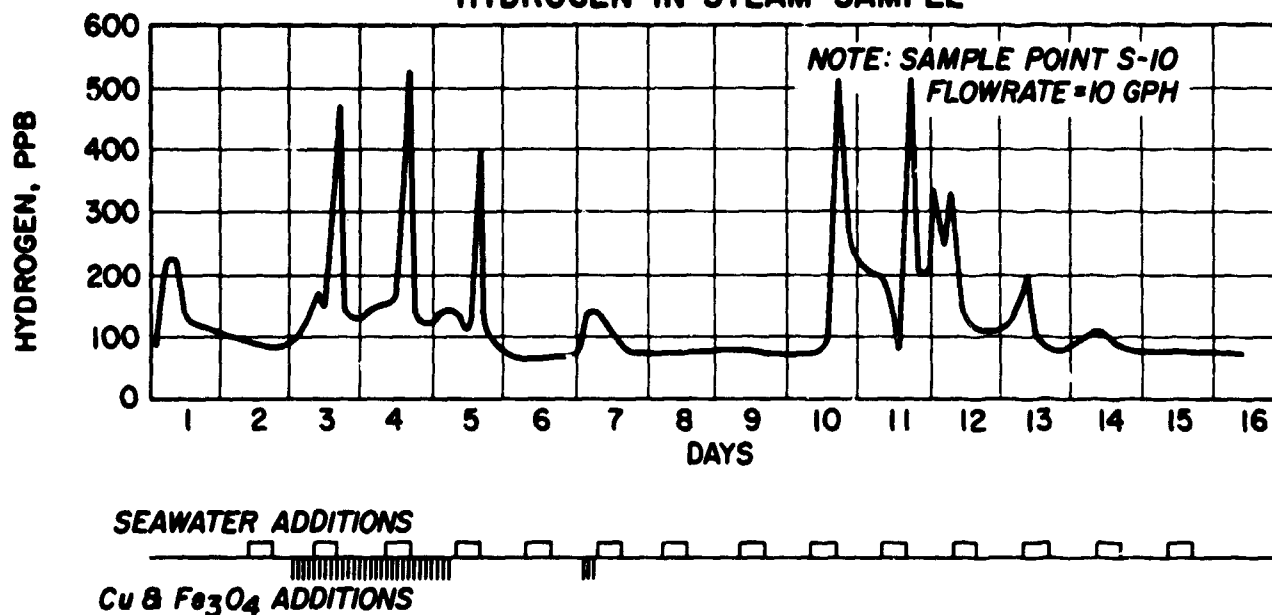
*Fig. 24: 250X photomicrograph of the deposit cross section from Test 2C*



*Fig. 25: Upper—250X photomicrograph of test section tube metal after Test 2C*

*Lower—100X photomicrograph of test section tube metal after tensile test.*

### TEST 3C PHASE III 10/16/66 - 10/31/66 HYDROGEN IN STEAM SAMPLE



### TEST 3C PHASE III 10/16/66 - 10/31/66 TUBE CROWN TEMPERATURE RISE

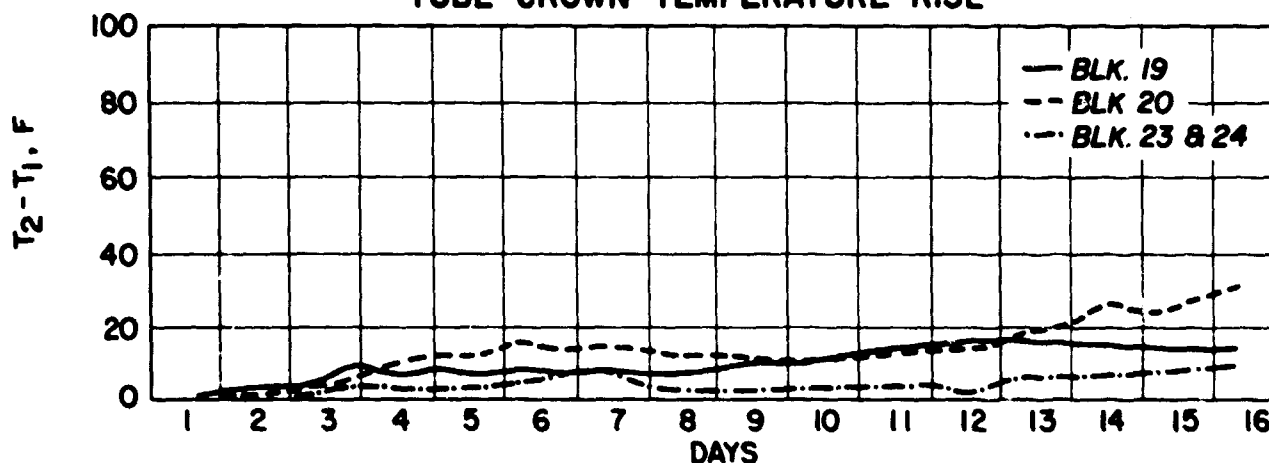


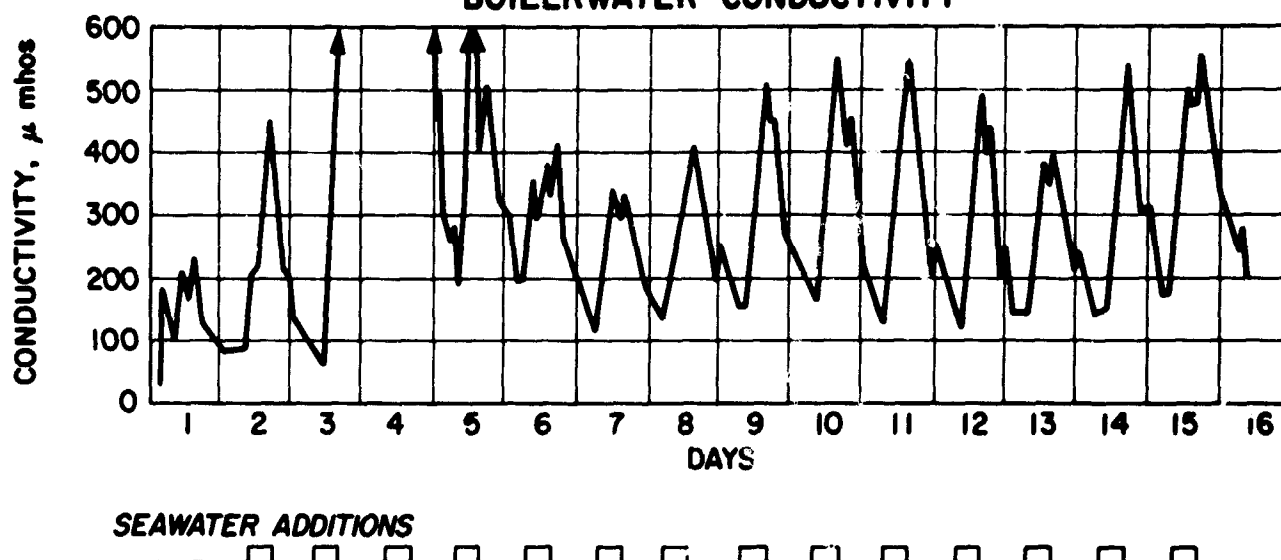
Fig. 26

suggest that differences in the chemistry of the system (with fresh-water condenser leakage) prevented the formation of stable deposits of preboiler corrosion products.

Data from the three tests with seawater condenser leakage showed that deposition on heat transfer surfaces was greater than during the fresh water tests. This is in accord with the relative quantities of hardness salts in the respective contaminant solutions. Deposition of corrosion products did not appear to be significantly greater, however, they were found to play a key role in the initiation of caustic attack as well as other types of corrosion during this group of tests. These results are discussed in detail in the section on corrosion.

During both the fresh water and seawater contaminant tests, frequent samples were taken to determine the insoluble phases formed. It is worthy of note that with but one exception no precipitated hardness was detected in large samples (8 to 10 liters) filtered through either 0.1 or 0.45 micron pore size filters. The exception occurred during the run with volatile treatment and seawater condenser leakage when magnesium hydroxide was found on the filters. All of the deposits removed from the heat transfer surfaces contained precipitated salts. The results indicated that precipitation of calcium and magnesium compounds occurred at the heat transfer surfaces or within the matrix of deposit on the surfaces rather than in the bulk boiler water.

**TEST 3C PHASE III 10/16/66 - 10/31/66  
BOILERWATER CONDUCTIVITY**



**TEST 3C PHASE III 10/16/66 - 10/31/66  
BOILERWATER pH**

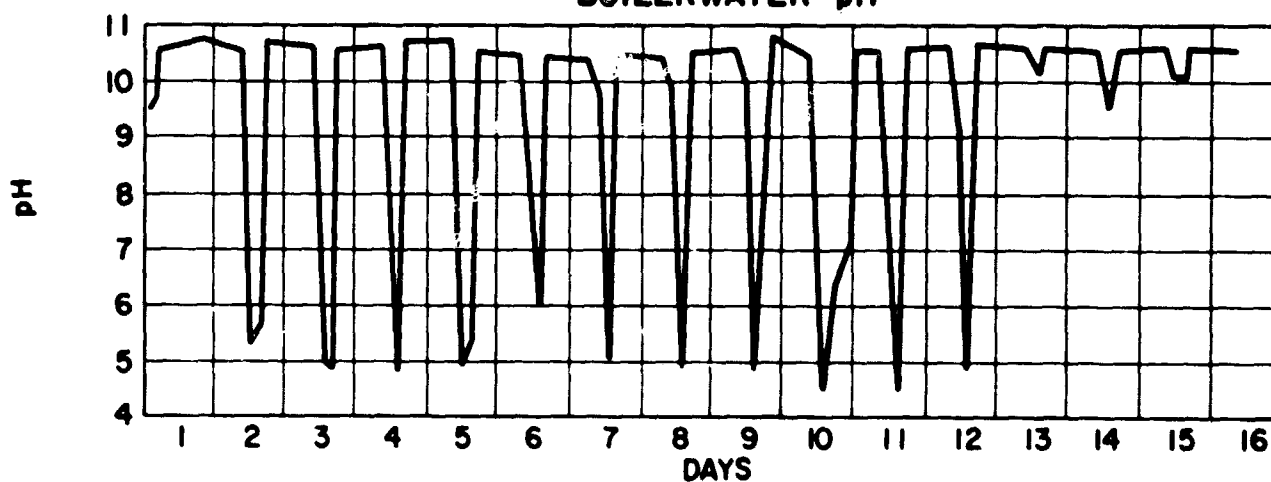


Fig. 27

Deposits formed during tests with condenser leakage were generally of a mixed matrix of iron oxide, copper, and precipitated salts. In attempting to chemically clean the specimens for surface examination, it was found that removal of deposits was frequently difficult even where magnetite was a major constituent. The deposits from two volatile treatment runs were extremely difficult to remove with hot (160 F) inhibited hydrochloric acid (5 percent), thiourea (1 percent), and ammonium bifluoride (0.5 percent) solution, even with a great deal of surface agitation. Cleaning the surfaces of specimens from the coordinated-phosphate test with seawater leakage was also very difficult. In each case the problem of deposit removal seemed to be related to

the complex matrix of the material and the relative dissolution rate of its component parts. The less soluble materials prevented adequate contact between the acid solution and the more soluble constituents. Much of these deposits finally flaked loose from the metal surface instead of entering the solvent solution. Another interesting observation was that the composition of the drum deposits bore little similarity to those found on the heat transfer surfaces. Drum deposits generally consisted of gravity-separated iron oxide and copper, and frequently contained no detectable concentration of precipitated salts, whereas the latter formed a significant portion of the deposits on the heat transfer surfaces of both the preheat and test sections.

TEST 3C PHASE III  
PHOSPHATE WIDEOUT

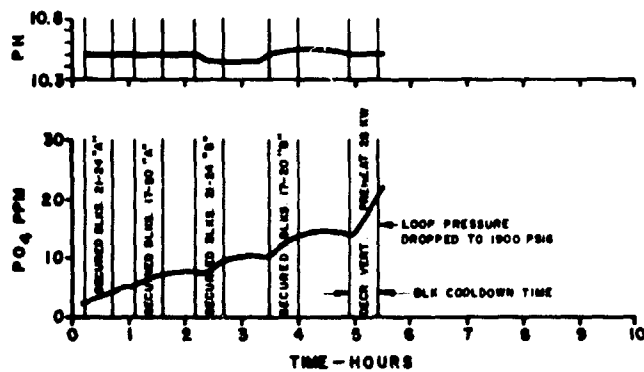


Fig. 28

### Corrosion

Inspection of tube specimens from three tests performed with both fresh-water condenser leakage and corrosion product contamination revealed that no detectable corrosion had occurred. This absence of corrosion under severe heat transfer conditions in the presence of these contaminants may be explained by the nature of the observed deposits and the concurrent boiler water chemistry.

The most obvious effect of the addition of fresh-water condenser leakage during the volatile run was an elevation in pH from the range of 8.6 to 9.0 to approximately 10.0; the increase resulted from the thermal decomposition of the bicarbonates added to the boiler water. Calcium precipitated at the heat transfer surfaces and deposited, primarily, as calcium sulfate. Magnesium compounds in the deposits were not present in sufficient concentration for positive identification. The net result of the injection of moderate amounts of this type of condenser leakage was, therefore, a change in boiler water chemistry from "zero solids" volatile treatment to a low-level free-caustic treatment with neutral salts in solution (sodium sulfate and sodium chloride). This chemistry, in conjunction with the relatively thin, dense deposits formed, and the resulting moderate increase in tube metal temperature (30 F), did not constitute an aggressive environment.

The results of the coordinated-phosphate test were similar, with the exception that calcium and magnesium precipitated as phosphates. The calcium-phosphate reaction resulted in higher concentrations of sulfates in solution than during the volatile run. The simulation of condenser leakage, in effect, only constituted a change in boiler water chemistry from coordinated-phosphate to low-caustic phosphate treatment with higher total solids. No significant change in pH was experienced. This combination of water chemistry, the relatively thin loose deposits, and a resulting 20 F increase in tube metal temperature was not corrosive to tube metal.

The last test in this series was run with free-caustic, low-phosphate treatment. The results were much the same as those from the coordinated-phosphate run with the exception of the greater amounts of free caustic alkalinity in the boiler water and the depletion of the entire phosphate residual during periods of simulated condenser leakage.

The absence of gouging attack, such as that experienced in a prior caustic test, appears most closely related to the formation of deposits, although other factors play a part. The data from the earlier test, which was run under similar conditions but without simulated condenser leakage, reveal that substantial deposits formed immediately upon the injection of corrosion products into the loop. These deposits were sufficiently stable to sustain an elevated tube-metal temperature and a correspondingly high corrosion rate for periods in excess of one day after each group of contaminant injections. Comparisons of these temperature and hydrogen data with those from the tests with

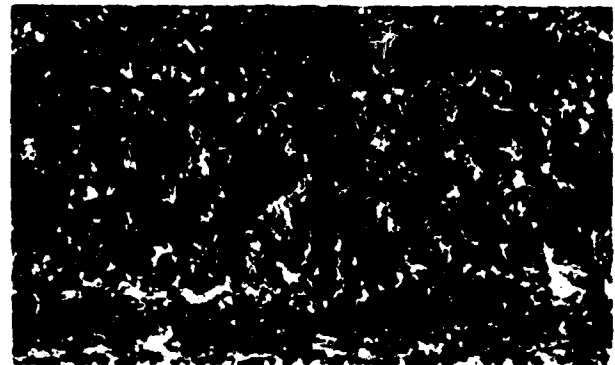


Fig. 29: Upper—Appearance of deposits formed on tube surfaces during Test 3C

Lower—Tube surface after removal of deposits by chemical cleaning

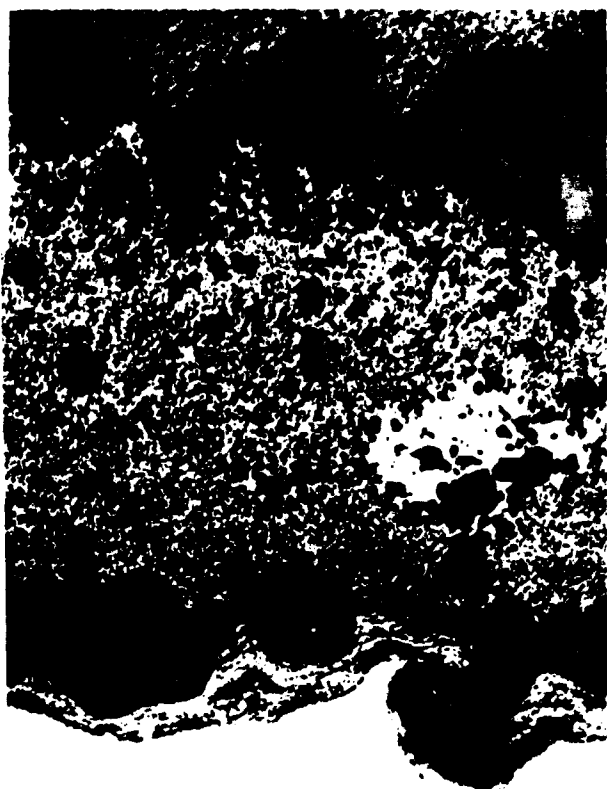


Fig. 30: 100X photomicrograph of the deposit cross section from Test 3C

fresh-water condenser leakage revealed significant differences. During the latter, each addition of iron oxide and copper resulted in only minor increases in tube-metal temperature and hydrogen concentration, followed by rapid decreases in these values.

The introduction of fresh-water condenser leakage appears to have reduced the deposition of iron oxide and copper contaminants, thereby minimizing the equilibrium concentration of caustic and other salts at the deposit-metal interface. The presence of substantial concentrations of neutral salts in solution would also tend to minimize the caustic concentration occurring within the deposit by a dilution effect. These factors appear to be primarily responsible for the absence of gouging-type attack during all three fresh-water condenser-leakage runs. The test results do not indicate that these conditions would produce any other characteristic type of corrosion.

Examination of tube specimens from three tests with simulated seawater condenser leakage revealed that corrosion in varying degrees had occurred during each run. The data shows that attack, resulting directly from the addition of seawater contaminant, occurred only after the residual buffer had been depleted during the coordinated-phosphate and free-caustic runs. During the volatile test, however, corrosion progressed independent of the presence of ammonia. The data from

each test revealed the importance of the deposits with respect to the initiation of corrosion. It was found that a pH excursion (4.5 to 5.0) resulting from the injection of seawater leakage did not result in an increase in corrosion rate until the heat-transfer surfaces had become fouled with deposits. During these tests the initial fouling resulted from the addition of corrosion product contaminants.

The results of the caustic test are of particular interest since on some days high rates of hydrogen evolution occurred alternately in both the acid environment created by the seawater injection and the alkaline environment produced by boiler water control with sodium hydroxide. The phenomenon is defined by the pH and hydrogen data from this test. The data also shows that increases in hydrogen concentration did not always accompany pH excursions nor did significant reductions in pH occur with each seawater injection. These exceptions to the normal pattern are not clearly understood.

Test data (principally from the volatile test) indicate that pH excursions and the accompanying corrosion occurred as a result of the reaction of magnesium ions with boiler water. In the absence of a residual buffer, magnesium precipitated as magnesium hydroxide, thereby reducing the hydroxyl ion concentration in the boiler water. This reaction resulted in an effective reduction of the bulk water pH to approximately 4.5. Since ammonia remains virtually undissociated at the operating conditions of these tests (2600 psia, 674 F) its injection to control pH provided no effective buffering and, therefore, the reaction of magnesium with the boiler water continued to be the controlling phenomenon. In the cool boiler water sample, dissociated ammonia provided sufficient hydroxyl ion concentration for complete precipitation of the soluble magnesium and an elevation of the sample pH to the control range. Reduction of the corrosion rate of the metal surfaces was not accomplished until the salt concentration of the boiler water was sufficiently depleted by blowdown. The introduction of either sodium phosphate or sodium hydroxide during subsequent tests were effective in controlling attack without significant blowdown under similar conditions.

## CONCLUSIONS

Based upon the results of the entire research program, the following conclusions have been made:

1. Deposition of boiler water contaminants, both simulated preboiler corrosion products and condenser leakage, occurred primarily on the heated portions of the test surfaces.
2. With few exceptions, preboiler corrosion products deposited from suspension.

3. Most condenser leakage constituents precipitated and deposited at the heat-transfer surfaces rather than in the bulk stream.
4. The amount and location of preboiler corrosion-product deposition was affected by boiler water treatment and the presence of condenser leakage.
5. Deposition of preboiler corrosion products was greater in the A loop (23 to 35 percent quality) than in the B loop (8 to 20 percent quality) at identical conditions of water chemistry, heat flux, mass velocity, and pressure. The formation of deposits resulting from condenser leakage was not appreciably affected by mixture quality; approximately equal amounts of these materials having been found at similar locations in both the A and B loops.
6. Within a four-block test section, deposition of preboiler corrosion products increased with mixture quality at constant heat flux (i.e., block 20 > 19 > 18 > 17 and block 24 > 23 > 22 > 21). Deposition of condenser leakage constituents was not clearly affected by increasing mixture quality within each section.
7. Within each test section, the deposition of both preboiler corrosion products and condenser leakage was greater in the high-heat-flux zone (blocks 17 to 20, 150,000 Btu hr-ft<sup>2</sup>) than in the low-heat-flux zone (blocks 21 to 24, 110,000 Btu hr-ft<sup>2</sup>).
8. Volatile treatment permitted the formation of difficult to remove deposits. The deposits formed with this type boiler water treatment had higher concentrations of precipitated hardness and silicon compounds than with coordinated phosphate or free caustic boiler water.
9. Coordinated phosphate and free caustic treatment reduced the amount of deposition and resulted in less objectionable deposits from the standpoint of cleaning when fresh-water condenser leakage was introduced to the test boiler.
10. In all cases, when corrosion was experienced, prior fouling of heat-transfer surfaces was necessary for the initiation of attack. When heat-transfer surfaces were free of deposits, no corrosion occurred independent of heat-transfer conditions and water chemistry.
11. When either volatile or phosphate treatment was employed with tube surfaces fouled with preboiler corrosion products and in the absence of condenser leakage, no significant corrosion occurred.
12. The combination of heat-transfer surfaces fouled with simulated preboiler corrosion products and free caustic boiler water treatment caused high rates of corrosion under nucleate boiling conditions.
13. The initial deposition of preboiler corrosion products on heated tube surfaces initiated caustic attack. Subsequent formation of additional deposits resulting from corrosion of the metal sustained and finally accelerated the corrosion rate.
14. Plug-type corrosion occurred with volatile boiler water treatment when heat-transfer surfaces were fouled with preboiler corrosion products and seawater condenser leakage was added. Volatile treatment furnished no protection against corrosion resulting from seawater leakage.
15. The pH reduction of boiler water resulting from seawater condenser leakage caused corrosion with all types of chemical treatment. However, corrosion rates could be effectively reduced by elevating the pH with sodium phosphate or sodium hydroxide. Once the heat-transfer surfaces had become sufficiently fouled, the introduction of sodium hydroxide to arrest seawater corrosion resulted in caustic attack.
16. Phosphate hideout became more pronounced with the accumulation of deposits on heat-transfer surfaces. No corrosion was associated with its occurrence.
17. The chemical composition of deposits on heat-transfer surfaces varied significantly from those found on unheated areas.
18. Deposition of contaminants resulted in DNB where nucleate boiling had been experienced with clean test surfaces. This effect was temporary since it was observed that the depressed value of critical quality recovered over a period of several hours subsequent to the addition of contaminant.